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'Reichenbach' and 'Brezina' lamellae in meteoritic irons.

(With Plate XIII.)

By L. J. Spencer, C.B.E., M.A., Sc.D., F.R.S.

Formerly Keeper of Minerals in the British Museum.

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BARON Karl Ludwig von Reichenbach (1788–1869) was born at Stuttgart, ennobled in 1839 by the King of Württemberg, and died at Leipzig. But he spent most of his life in Austria, where he had iron works and estates in Moravia and Galicia and a castle near Vienna. Earning a livelihood as a copyist in the state archives, he was able to obtain a university education, and he started his career as a works chemist. He produced many papers on the distillation products of coal, tar, oil, &c., and was the discoverer of creosote and solid paraffin. He gained considerable notoriety with his ideas and books on what he called 'od' or 'odylic force', a combination of animal magnetism, light, heat, force of crystallization, &c., capable of producing hypnotism. The fall in 1833 of a shower of meteorites, which he witnessed near his works at Blansko in Moravia, fired his intense enthusiasm for the subject of meteorites, on which he wrote 29 scientific papers (1835–65) and many newspaper articles. The well-known names kamacite, taenite, and plessite[1] for the nickel-iron constituents of meteorites are due to him. In 1861 he observed bands of iron sulphide in the Widmanstetter pattern on etched surfaces of three meteoritic irons from Lenarto (Slovakia), Caille (La Caille, France), and Claiborne (now known as

[1] K. L. Reichenbach, Ueber das innere Gefüge der nähern [näheren] Bestandtheile des Meteoreisens. Ann. Phys. Chem. (Poggendorff), 1861, vol. 114, pp. 123, 252, 269, respectively.

Walker County, Alabama).[1] The best example was Claiborne 'das ich im brittischen Museum fand'. His collection of meteorites was bequeathed to the University of Tübingen, making it at that time the best in Germany.[2]

Similar bands of troilite were independently observed by G. Tschermak[3] in 1871 in a meteoritic iron from the Atacama Desert (Ilimaes) and in those from Jewell Hill (Duel Hill, North Carolina) and Victoria West (South Africa). He described them as due to lamellae oriented parallel to cube planes in the octahedral structure, and cutting across the lamellae of kamacite and taenite. A. Brezina[4] in 1880 applied the name *Reichenbach lamellae* (Reichenbach'sche Lamellen) to lamellae of troilite oriented on cube planes, and described other examples in Staunton (Virginia); Trenton (Wisconsin), Juncal (Chile), and Ruff's Mountain (South Carolina).

A. Brezina and E. Cohen in 1887, in their album of photographs,[5] gave a picture of Knoxville (Tazewell, Tennessee) showing bands perpendicular to the edges of equilateral triangles. These were at first thought to represent Reichenbach lamellae of troilite. It was afterwards realized that with such a direction of the bands the lamellae must be parallel to planes of the rhombic dodecahedron and not of the cube. Also it was found that in the centre the bands consisted of schreibersite. In 1898 E. Cohen[6] described the same orientation of schreibersite in Ballinoo (Western Australia). In 1904 A. Brezina[7] completed his account of this

[1] K. L. Reichenbach, loc. cit., 1861, vol. 114, p. 114; 1862, vol. 115, p. 630.

[2] F. A. Quenstedt, Die Meteoriten der Tübinger Universitätsammlung. Geschenk des Freiherrn v. Reichenbach, 1871, 4 pp. S. Blattmann and F. Machatschki, Stand der Tübinger Meteoritensammlung mit Ende 1937. Neues Jahrb. Min., Abt. A, vol. 74, pp. 279–292. [M.A. 7–265.]

[3] G. Tschermak (1836–1927), Ein Meteoreisen aus der Wüste Atacama. Anzeiger Akad. Wiss., Math.-naturwiss. Cl., Wien, 1871, vol. 8, p. 28 (abstract); the full paper in the Denkschriften, 1872, vol. 31, pt. 1, pp. 187–196, 4 pls. Meteoreisen von Victoria West. Min. Mitt., 1872, Jahrgang 1871, p. 109; also in Jahrb. Geol. Reichsanstalt, Wien, 1872, vol. 21 (for 1871).

[4] A. Brezina, Über die Reichenbach'schen Lamellen in Meteoreisen. Anzeiger, Wien, 1880, vol. 17, pp. 177–178 (abstract); the full paper in the Denkschriften, 1882, vol. 43, pt. 2, pp. 13–16, 4 pls. Preprints, pp. 1–4, 4 pls., dated 1880.

[5] A. Brezina and E. Cohen, Die Struktur und Zusammensetzung der Meteoreisen, erläutert durch photographische Abbildungen geätzter Schnittflächen. Stuttgart, 1887, parts II–III, pls. X and XI.

[6] E. Cohen, Über ein neues Meteoreisen von Ballinoo am Murchisonfluss, Australien. Sitz.-ber. Akad. Wiss. Berlin, Phys.-math., Cl., 1898, no. II, pp. 19–22.

[7] A. Brezina, Über dodekaedrische Lamellen in Oktaedriten. Sitz.-ber. Akad. Wiss. Wien, Math.-naturwiss. Kl., 1904, vol. 113, Abt. I, pp. 577–583, 1 pl.

structure, giving additional examples in Narraburra (New South Wales),[1] Augustinovka (Ukraine), and Joe Wright (Joe Wright Mountain, Arkansas). Finally, in 1905, E. Cohen[2] proposed the term *Brezina lamellae* (Brezina'sche Lamellen) for lamellae of schreibersite oriented on planes of the rhombic dodecahedron.[3]

Reichenbach and Brezina lamellae have since been mentioned in several other meteoritic irons. They show a scattered and irregular distribution on the etched surfaces. Only exceptionally are the full number of cube and dodecahedral planes represented. The bands are 1–3½ cm. long and 0·1–1 mm. wide, and are usually not very conspicuous, especially in published reproductions of photographs of the etched surfaces. They cut across the bands of kamacite and taenite of the Widmanstetter pattern causing no distortion; and it has been suggested that they crystallized before the nickel-iron. A disconnected network of lamellae could, however, scarcely have controlled the subsequent orientation of the nickel-iron. More likely they crystallized out together as regular intergrowths.

The term Shepard lamellae (Shepard's lamellae)[4] has been applied to lamellae of schreibersite ($(Fe,Ni)_3P$) on (111) [possibly (100)]. Other orientations of schreibersite on (100), (210), (211), or (221) have been described by G. F. Kunz and E. Weinschenk, 1892; O. B. Bøggild, 1927 [M.A. **3**–535]; F. Heide, E. Herschkowitsch, and E. Preuss, 1932 [M.A. **5**–300]; W. Borchert and J. E. Ehlers, 1934 [M.A. **6**–11]; R. F. Mehl, C. S. Barrett, and H. S. Jerabek, 1934, in manufactured iron [Min. Mag. **26**–163]. Troilite (FeS) on (110) has been described by F. Rinne, 1910. Cohenite (Fe_3C) on (111) by E. Weinschenk, 1889; and on (110) by C. W. Beck, L. LaPaz, and L. H. Goldsmith (Min. Mag., 1951, vol. 29, p. 531). A search of the literature would no doubt yield other examples.

The question now arises whether the term 'Reichenbach' lamellae should still be retained for troilite oriented on the cube, and 'Brezina' lamellae for schreibersite oriented on the dodecahedron, or whether the terms should apply to a particular mineral or to a particular orientation.

[1] A. Liversidge, The Narraburra meteorite. Journ. Roy. Soc. New South Wales, 1904, vol. 37, pp. 234–242, 12 pls. The prominent bands are figured, and the high phosphorus shown in the analysis suggested schreibersite.

[2] E. Cohen (1842–1905) Meteoritenkunde, Heft III. Stuttgart, 1905, p. 252.

[3] Dr. Maria Aristides Brezina (1849–1909) had charge of the collections of minerals and meteorites in the Natural History Museum at Vienna. [Min. Mag. **15**–442.]

[4] J. D. Buddhue, Meteoritic iron phosphide. Popular Astronomy, 1938, vol. 46, pp. 282–285; Contr. Soc. Res. Meteorites, [1939], vol. 2, no. 1 (for 1938), pp. 40–43. [M.A. **7**–172.]

Three minerals and six orientations, mentioned in the last paragraph, would give eighteen possible combinations. To introduce a special name for each of these would be quite unnecessary and most undesirable. The orientation of troilite on cube planes has never been rigidly proved, but its orientation on dodecahedral planes is demonstrated by the examples to be described below and illustrated in pl. XIII.

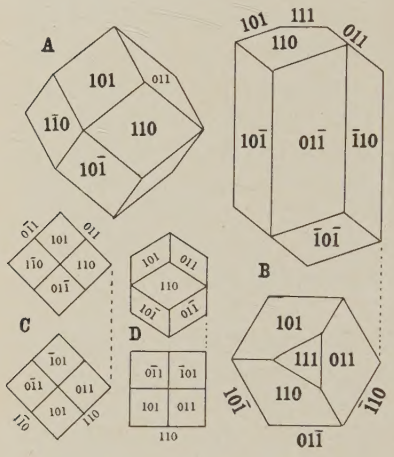

FIG. 1.

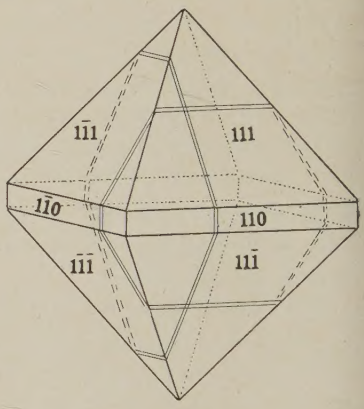

FIG. 2.

FIG. 1. Rhombic dodecahedron. A, clinographic projection. B–D, orthographic projections (plans and elevations); B with a triad axis vertical and elongated along this axis; C and D with a tetrad axis vertical.

FIG. 2. Octahedron with enclosed lamellae parallel to two faces of the rhombic dodecahedron.

It is strange that Tschermak made no mention of Reichenbach and that neither of them made any mention of Schreibers,[1] who briefly described and figured these lamellae as early as 1820, but wisely without guessing at the mineral or the orientation. Lamellae of any mineral in any orientation might appropriately be called Schreibers lamellae. But,

[1] Carl von Schreibers (1775–1852), Beyträge zur Geschichte und Kenntniss meteorischer Stein- und Metall-Massen . . . Wien, 1820, p. 76, pl. VIII. The lamellae are shown on an etched slice from the 39 kg. mass which fell in 1751 at Hraschina near Agram (= Zagreb) in Croatia, and preserved in the Vienna Museum. Mention of this was made by A. Brezina in his 1885 catalogue (p. iv) of the Vienna collection of meteorites; that is, five years after he had proposed the name Reichenbach lamellae. He mentions troilite oriented on the cube, but gives no fresh description. E. Cohen (Meteoritenkunde, 1894, I, p. 189) refers doubtfully to Schreibers's observation.

as now shown, 'Reichenbach' lamellae of troilite have the orientation that was allotted to schreibersite in 'Brezina' lamellae. The best course now would be to retain the term Reichenbach and reject all others.

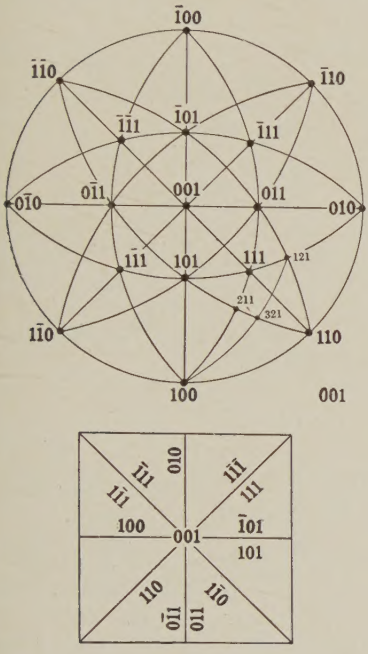

Fig. 3.

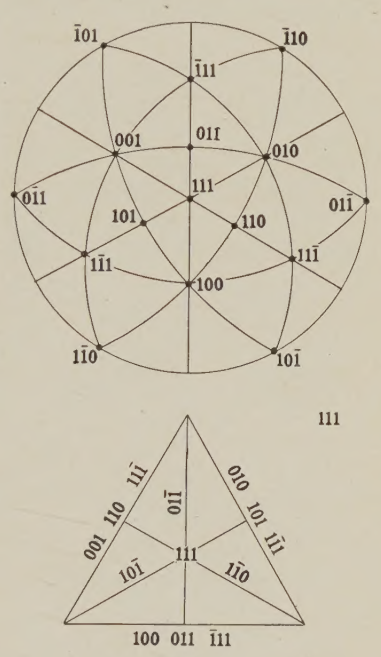

Fig. 4.

Figs. 3 and 4. Stereographic and orthographic projections on (001) and (111).

When the bands shown on an etched surface are at right angles it has frequently been assumed that they represent lamellae parallel to cube planes. This is not necessarily the case, and on a section parallel to an octahedral plane it is only possible when the lamellae are parallel to planes of the rhombic dodecahedron.

The usual clinographic drawing (fig. 1A) of a rhombic dodecahedron gives some idea of the general shape, but when drawn in other positions it presents quite different aspects (figs. 1B–D). This polyhedron is bounded by four hexagonal zones, each perpendicular to an octahedral face. In fig. 1B one of these hexagonal zones is emphasized by elongation along a triad axis; and it is clear from the plan that intersections on the octahedral face are parallel and perpendicular to octahedral edges. The

same effect is illustrated in fig. 2, showing lamellae parallel to (110) and $(1\bar{1}0)$ enclosed in an octahedron.

On any chance section of a meteoritic iron the directions of these lamellae in relation to the Widmanstetter pattern may be very puzzling.

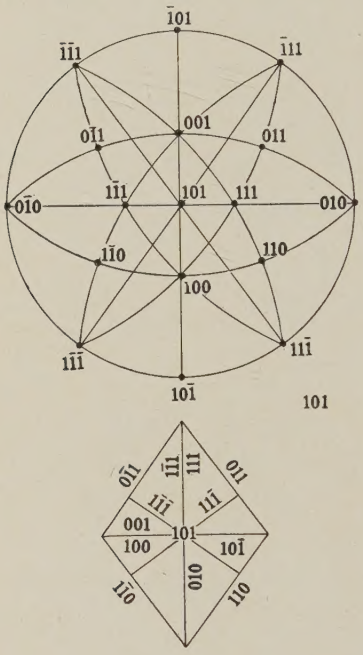

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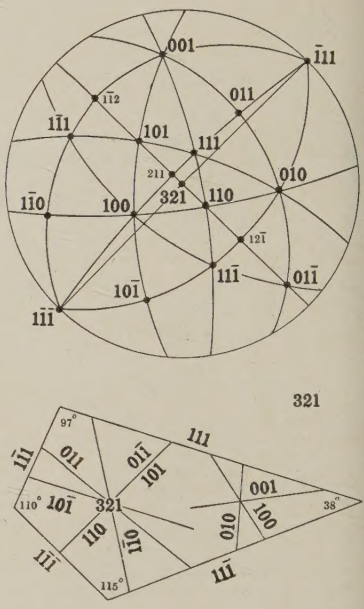
Fig. 5.



321

Fig. 6.

Figs. 5 and 6. Stereographic and orthographic projections on (101) and (321).

The Widmanstetter pattern itself is symmetrical only when the section plane is perpendicular to an axis of symmetry or parallel to a plane of symmetry. But we may continue our lesson in elementary crystallography if we limit ourselves to the principal planes (100), (111), and (110). Figs. 3–5 show in stereographic and orthographic projections the several combinations with these three crystal-forms as section planes. The general case for any chance section not lying in a plane of symmetry yields thirteen directions of intersection with (100), (111), and (110). The example shown in fig. 6 with (321) as the section plane yields only eleven directions, because this face falls in a hexagonal zone with three faces of the rhombic dodecahedron.

In fig. 7 the directions have been sorted out for each crystal-form, with the addition of those for the icositetrahedron (211). This form has been mentioned as a possible orientation of lamellae, and it is of importance in giving the directions of Neumann lines in kamacite. Figures for these

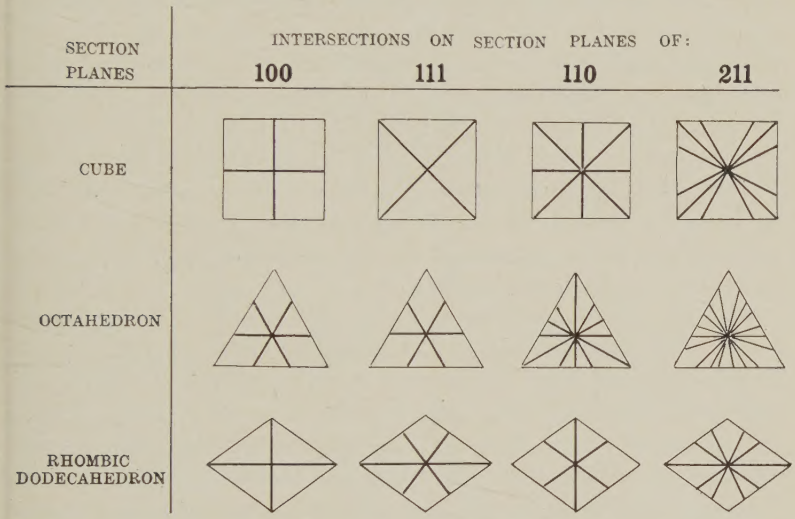


FIG. 7. Intersections of (100), (111), (110), and (211) lamellae on section planes (100), (111), and (110).

have previously been given in this Magazine.[1] On the cube face there are six directions of intersection, on the octahedron nine, and on the rhombic dodecahedron five. For any chance section not lying in a symmetry zone the number is twelve. The general form (*hkl*) would give 24 directions on a chance section plane.

In addition to the right angles shown in fig. 7, there is an infinite number of sections of the octahedron that give this angle. Demonstrating with templets ('jigs'), my grandson Benjamin Barman has pointed out to me that a templet of 90° can be applied to adjacent faces of an octahedron in two ways. (1) It can slide down the edge, while keeping parallel to a cube face, all the way to the adjacent cube pole, the limbs of the templet then coinciding with dodecahedral edges or axes of symmetry.

[1] L. J. Spencer, A new meteoric iron from Piedade do Bagre, Minas Geraes, Brazil. Min. Mag., 1930, vol. 22, pp. 271–282, 2 pls. Under fig. 4 *b*, p. 277, the number of intersections on a cube face is there incorrectly given as ten; the figure actually shows four parallel pairs, thus reducing the number to six.

This gives the square Widmanstetter pattern shown on a section parallel to a cube face. (2) Contact can also be obtained by rotating the templet as it moves along the edge. Starting from a cube pole with the templet parallel to a cube face (and inclined at 45° to the edge) it will, when half way down the edge, be parallel to an octahedron face. With a clockwise rotation the limb on the right-hand face, after moving 30° over that face, is parallel to the edge; while that on the left-hand face, after moving 60°, is perpendicular to the edge (compare fig. 2). An anti-clockwise rotation reverses these angles and directions. Now turn the templet over and travel down the lower half of the edge. There will be a repetition of the same performance, but in reversed order, and ending up parallel to the cube face of the adjacent pole. The half-way position along the edge marks the passage over a dodecahedral plane of symmetry and over a dyad axis of symmetry.

Between the cube and octahedron faces the templet (representing the section plane of the meteorite) has not been travelling perpendicularly to a dodecahedral plane of symmetry, but along a path of hexakisoctahedra with high indices and not in a zone. In fig. 6 I found graphically an angle of 97° for the face (321). An irregular four-sided templet with one angle of 90° and others of 40°, 112°, and 118° was found to fit on the octahedron. Brezina[1] in a table of calculated angles between kamacite bands in the Widmanstetter pattern on section planes of an octahedrite gives for (421) an angle of 90°. Planes deviating but slightly on either side of this position show a departure from this angle: for (454.200.100) he gives 91·7°, and for (742) 87·2°, on either side of (421). He also gives angles of 90° for (64.8.1), (16.4.1), (931), (964), (25.20.6), and (121.110.100), some of which may perhaps fall in this field. Avoiding elaborate calculations, I have assumed when drawing fig. 8A a gradual deviation of the section planes from the dodecahedral planes of symmetry along curved paths (represented by small circles on the stereographic projection), choosing for the maximum deviation a point mid-way between (100) and (111): for (421), angle to (100) 29° $14\frac{1}{4}'$, to (111) 28° $6\frac{1}{2}'$, and angle (421) : (412) 17° $45\frac{1}{4}'$. One curve from (100) passes through (421), turns at (111), and through (241) reaches (010); the other through (412), (111), and (214) to (001). At the limiting position (111), corresponding with the critical point half way down the octahedral

[1] A. Brezina, Meteoritenstudien II. Über die Orientirung der Schnittflächen an Eisenmeteoriten mittelst Widmannstädten'schen Figuren. Denkschr. Math.-naturwiss. Cl. Akad. Wiss. Wien, 1882, vol. 44, pp. 121–158, 5 pls. Preprints, pp. 1–38, 5 pls.. dated 1881.

edge, the (*hkl*) faces coalesce with (111), and the section plane then gives the triangular Widmanstetter pattern. At the opposite limit they coalesce with cube faces, giving the square pattern.

Fig. 8B gives the directions of intersection of octahedral planes on a section plane (421). These directions and angles can be arranged in

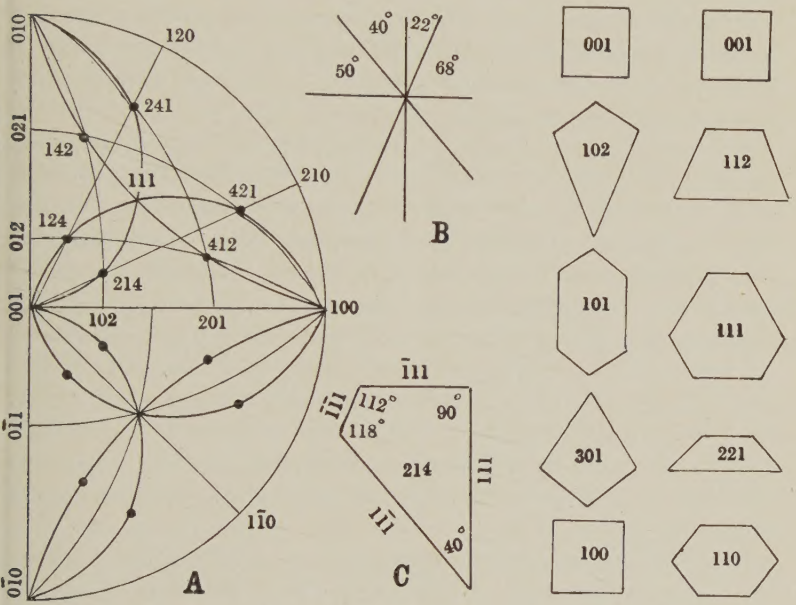


Fig. 8 Fig. 9

Fig. 8. A, Loci of oblique section planes of an octahedron giving angles of 90°. B, Directions of intersection of octahedral planes on (421), with an angle of 90°. C, Shape of section plane of an octahedron by (421).

Fig. 9. Series of sections of an octahedron by planes perpendicular to cubic and dodecahedral planes of symmetry.

several ways to give closed polyhedra of different shapes (see Min. Mag., 1941, vol. 26, p. 29, fig. 5). One of them (fig. 8c) cut as a templet can be fitted over each of the six apices of the octahedron in two positions (with reversal of the templet).

Another form of templet devised by B. Barman consists of two hinged right angles. A modification of this in the form of a deltoid with angles 90°, 90°, 45°, 135° (or an octagon with angles 135°) fits to the rhombic dodecahedron and cubo-octahedron, but not to the octahedron. This

gives the cubo-octahedral [or dodecahedral] pattern (pl. XIII, fig. 3) of F. Rinne.[1] Deltoidal templets with angles 90°, 90°, 30°, 150° and 90°, 90°, 60°, 120° were cut in an attempt to solve the new type of pattern presented by the La Porte meteorite.[2] But these do not fit the dodecahedron, octahedron, or spinel twin. The hinged templet of two right angles gave no further result, except parallel to cube faces.

Still more templets were cut to represent sections of the octahedron by section planes perpendicular to the cubic and dodecahedral planes of symmetry in positions ranging from (001) to (100) and (001) to (110). The shapes of these sections are represented in fig. 9.

Actual specimens of meteorites showing really good examples of these lamellae, and giving conclusive evidence of the orientation, are quite rare. A preliminary search of the literature for photographic reproductions has also given but few good examples. With the scattered and usual absence of the full number of bands it is not always possible to distinguish between orientations on the cube and the dodecahedron. On a cube section bands at 45° to the kamacite bands may be due to either; but bands at 0° (or 90°) and 45° can be due only to the dodecahedron (pl. XIII, figs. 1 and 3). On an octahedral section bands at 0° may be due to the cube, octahedron, or dodecahedron; but bands at 0° and 90° are due only to the dodecahedron (pl. XIII, figs. 2 and 5). I have not yet found an example giving conclusive evidence of orientation on cube faces.

Plate XIII, fig. 1 shows a section parallel to a cube face of a siderite from the meteorite craters of Henbury in Central Australia. There can be no mistake here about the section being parallel to a cube face, for on the same specimen sections have been cut also parallel to octahedron and dodecahedron faces. The figure is reproduced from this Magazine,[3] and it is only now that the two stray bands of troilite have been specially noticed. One is parallel and perpendicular to kamacite bands, and the other at 45°. As shown by text-figs. 3 and 7 such an arrangement is only possible for lamellae parallel to the rhombic dodecahedron; and it does not conform with the original definition of Reichenbach lamellae of troilite on (100). The complete pattern should show four directions at

[1] F. Rinne, Ein Meteoreisen mit Oktaeder- und Würfelbau (Tessera-Oktaedrit). Neues Jahrb. Min., 1910, vol. i, pp. 115–117, 2 pls.

[2] S. K. Roy and R. K. Wyant, The La Porte meteorite, Geol. Ser. Field Museum Nat. Hist. Chicago, 1950, vol. 7, no. 10, pp. 135–144. [M.A. 11–271.]

[3] L. J. Spencer, Meteoric iron and silica-glass from the meteorite craters of Henbury (Central Australia) and Wabar (Arabia). Min. Mag., 1933, vol. 23, pp. 387–403, 8 pls.

45° and 90°. The two bands are not connected and they do not disturb the kamacite bands, suggesting that the troilite must have crystallized at the same time as the nickel-iron.

Fig. 3, pl. XIII, shows a section parallel to a cube face of a 404 kg. mass from Goamus farm,[1] of the Gibeon shower of meteorites in South-West Africa.[2] It shows three smaller bands of troilite parallel to kamacite bands and three larger bands at 45° to the same set of kamacite; all of them again isolated and not disturbing the kamacite. The larger troilite bands enclose white specks of schreibersite. This specimen is a rare example in which all four possible directions of troilite lamellae oriented on the dodecahedron are represented. It is also remarkable in showing four directions of the kamacite bands: two long (vertical) bands with associated shorter (horizontal) bands are shown in the upper part of the figure. Rinne regarded one set to be parallel to the cube and the other parallel to the octahedron, and he applied the name 'Tessera-Oktaedrit' (cubo-octahedrite) to this new type of meteorite. But taking the two sets together they represent lamellae parallel to the rhombic dodecahedron, and the type might better be named dodecahedrite.

Fig. 4, showing another section parallel to a cube face with kamacite bands in two directions at right angles, is reproduced from G. Tschermak's figure (loc. cit., 1871) of the Ilimaes (Atacama) meteorite. This shows five troilite bands in one direction (NE.–SW. in fig. 4) but only one in the other direction (NW.–SE.). It may be that other bands (parallel to the dodecahedron) also happen to be missing. There is in fact a small black line (at the left-hand side of the figure) parallel to kamacite bands. If this is troilite then the orientation must be dodecahedral and not cubic.

The remaining two figures on plate XIII are of sections approximately parallel to an octahedron face, with kamacite bands forming triangles almost equilateral. The Breece (New Mexico) meteorite, described in the last number of this Magazine,[3] shows bands of cohenite parallel and perpendicular to kamacite bands, and therefore representing lamellae oriented on the rhombic dodecahedron. They had at first been thought to be Reichenbach lamellae oriented on the cube. Fig. 2 is a reproduc-

[1] F. Rinne, 1910, loc. cit., pl. XV. Other figures show the cubo-octahedral structure more clearly with higher magnification, but no troilite bands.

[2] L. J. Spencer, The Gibeon shower of meteorites in South-West Africa. Min. Mag., 1941, vol. 26, pp. 19–35, 2 pls.

[3] C. W. Beck, L. LaPaz, and L. H. Goldsmith, The Breece, New Mexico, meteoritic iron. Min. Mag., 1951, vol. 29, pp. 531–537.

tion of a clearer figure given earlier by S. H. Perry,[1] who described the bands as Reichenbach lamellae of troilite (loc. cit., p. 17) oriented on the cube. Here the bands are much longer than usual, and it is one of the very few examples where they are in contact, forming a network; but only two of the six possible directions are represented.

Fig. 5 is a reproduction of a portion of one of the several figures given by A. Liversidge[2] of the Narraburra (New South Wales) meteorite. It shows large bands of schreibersite perpendicular and short ones parallel to octahedral edges. His analysis of the iron showed an unusually high percentage of phosphorus, but he only suggested the presence of schreibersite (3·61 %). It was E. Cohen (loc. cit., 1904) who determined the bands to be schreibersite and described them as 'Brezina' lamellae oriented on the dodecahedron.

The remarkable specimen of Walker County, Alabama, which Baron Reichenbach in 1861 'found in the British Museum', weighs 22 kg. = $48\frac{1}{2}$ lb.; it was purchased under the name of Claiborne from Henry Heuland in 1843. The baron promptly acquired the main mass of $40\frac{3}{4}$ kg. (38·338 kg. now in the Tübingen museum). A preliminary, long-delayed examination of the British Museum specimen shows a complex pattern of troilite bands in at least a dozen directions, suggesting an orientation on (211) and inviting further study.

[1] S. H. Perry, The metallography of meteoric iron. Bull. U.S. Nat. Mus., 1944, no. 184, vii+206 pp., 78 pls. (Fig. 4 on pl. 47, p. 167.) [M.A. 9–290.]

[2] A. Liversidge, The Narraburra meteorite. Journ. Roy. Soc. New South Wales, 1904, vol. 37, pp. 234–242, 12 pls. (Portion of pl. XXII.)

Explanation of Plate XIII.

Sections of meteoritic irons showing 'Reichenbach' and 'Brezina' lamellae.

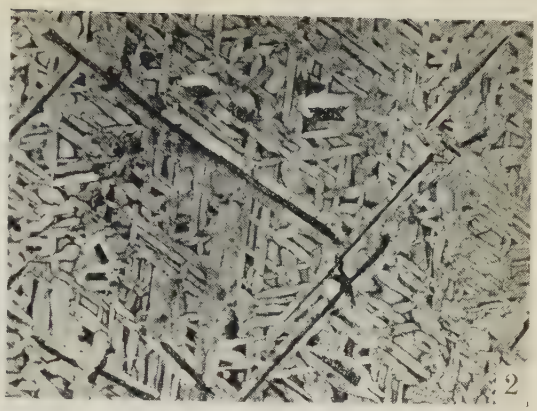
Fig. 1. Henbury, Central Australia. Section parallel to a cube face; bands of troilite oriented on rhombic dodecahedron. ×1·15. (L. J. Spencer, 1933.)

Fig. 2. Breece, New Mexico. Section parallel to an octahedron face; bands of cohenite oriented on rhombic dodecahedron. ×1·3. (S. H. Perry, 1944.)

Fig. 3. Goamus farm, Gibeon, South-West Africa. Section parallel to a cube face; bands of troilite and kamacite oriented on rhombic dodecahedron. ×$\frac{3}{4}$. (F. Rinne, 1910.)

Fig. 4. Ilimaes, Atacama, Chile. Section plane parallel to a cube face; bands of troilite oriented on cube [or possibly rhombic dodecahedron]. ×$\frac{2}{3}$. (G. Tschermak, 1871.)

Fig. 5. Narraburra, New South Wales. Section plane parallel to an octahedron face; bands of schreibersite oriented on rhombic dodecahedron. ×2. (A. Liversidge, 1904.)



L. J. SPENCER: 'REICHENBACH' LAMELLAE IN METEORITIC IRONS

The petrology of the evaporites of the Eskdale no. 2 boring, east Yorkshire.

Part III. *The upper evaporite bed.*

By F. H. Stewart, B.Sc., Ph.D., F.G.S.

With a chemical analysis by E. A. Vincent, B.Sc., A.R.I.C., F.G.S.

Department of Geology, Science Laboratories, University of Durham.

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I. Introduction and acknowledgements.

THE rocks of the lower and middle evaporite beds of the Permian, passed through by the D'Arcy Exploration Company's boring in 1938–39 (Lees and Taitt, 1946), have been described in earlier communications (Stewart, 1949, 1951). The present paper deals with the petrography of the upper evaporite bed (3655–3860 feet below surface). The material examined comprises:

Core samples of known depth collected by I.C.I. while drilling was in progress, and consisting of pieces of core, up to 6 inches in length and 4½ inches in diameter, taken at intervals of 2 feet in the following depth ranges: 3738–70, 3772–74, 3778–94, 3798–3816, 3818–30, 3838–42 feet below surface.

The uppermost 83 feet of the bed was not cored, so that there are no available samples from this depth range (3655–3738 feet). The range 3738–3820 feet is fairly well represented, but the lower 30 feet of the bed is represented by only two core samples.

Well cuttings taken at intervals of 5 to 10 feet, covering the whole depth range of the bed, and consisting of insoluble residues.

My sincere thanks are due to Imperial Chemical Industries and to the D'Arcy Exploration Company for supplying material for examination and for allowing me to use data obtained by them. The analytical details of KCl percentages were provided by I.C.I., and are quoted with their kind permission. I am indebted to the Durham Colleges for a research grant, and to Mr. G. O'Neill for taking the photographs which illustrate this paper.

II. The general succession.

		Thickness in feet.
	Saliferous marls.	
3655 feet		
	Not cored	83
3738 feet		
Zone of silty halite	Brown to colourless halite, with a considerable quantity of brown anhydritic silty material. A few flakes of talc, and traces of sylvine and carnallite.	18
	Reddish-brown to pink halite, with scarce silty material and anhydrite. A few flakes of talc and traces of sylvine and carnallite.	12
	Reddish-brown to pink halite, with a considerable quantity of brown anhydritic silty material. Talc abundant. Traces of carnallite.	14
	Pink, brown, and colourless halite, with small amount of brown anhydrite and silty material. A few flakes of talc, and traces of carnallite.	8
3790 feet		
Zone of granular halite (with scarce rinneite)	Pink granular halite with occasional layers and patches of coarse pink and colourless halite.	
	Contorted layers of anhydrite and anhydrite-halite-rock, with subordinate magnesite. No appreciable quantity of detrital material.	
	Significant amounts of sylvine and rinneite in specimens from 3802–3806 feet and 3824–3826 feet, and small quantities of these minerals in other samples.	44
3834 feet		
Anhydrite zone	Largely anhydrite, with subordinate magnesite and dolomite, and halite-anhydrite pseudomorphs after gypsum in samples from 3838 and 3840 feet.	
	Solution cavities in anhydrite cuttings suggest that pseudomorphs are present below these depths.	26
3860 feet		

As in the middle evaporite bed, polyhalite and kieserite are conspicuous by their absence. The range of halite in the lowest group is not known, since only two specimens were preserved. Neither do we know whether there is a potassium-bearing zone above the halite zone since the upper part of the bed was not cored. The well cuttings in this upper range consist of brown silt with some anhydrite, quartz, and a little magnesite and dolomite.

The distribution of potassium.

The details in the following table were provided by Imperial Chemical Industries. These figures are higher than those of the lower part of the middle evaporite bed. Each six-inch specimen was cut in half longitudinally, and the material for analysis scraped evenly from the flat surfaces so obtained.

Depth below surface in feet.	Total KCl %.	KCl % on water soluble material.	Depth below surface in feet.	Total KCl %	KCl % on water soluble material.
3738	0·48	0·52	3786	0·35	0·36
3740	0·41	0·53	3788	0·33	0·34
3742	0·51	0·62	3790	0·36	0·37
3744	0·41	0·43	3792	0·51	0·51
3746	0·54	0·59	3794	0·25	0·44
3748	0·42	0·48			
3750	0·32	0·45	3798	0·48	0·48
3752	0·60	0·66	3800	3·22	3·23
3754	0·59	0·77	3802	0·82	0·82
3756	0·30	0·33	3804	0·51	0·51
3758	0·48	0·48	3806	0·54	0·54
3760	0·35	0·35	3808	0·48	0·48
3762	0·36	0·36	3810	0·22	0·40
3764	0·40	0·40			
3766	0·30	0·30	3818	0·62	0·62
3768	0·30	0·37	3820	0·40	0·40
3770	0·36	0·48	3822	0·48	0·48
			3824	6·66	6·71
3778	0·40	0·41	3826	0·32	0·43
3780	0·48	0·51	3828	0·43	0·43
3782	0·36	0·39			
3784	0·30	0·33	3838	0·08	0·42

III. Rocks of the anhydrite zone.

The two available specimens are from near the top of this range (3838 and 3840 feet). They consist of alternate layers of light grey anhydrite-magnesite-rock and anhydrite-magnesite-halite-rock with pseudomorphs after gypsum, the layers being up to one inch thick, roughly horizontal, but wavy and contorted. Brown layers, a few millimetres in thickness, consisting largely of magnesite, are frequent. Quartz is present in small quantity. Detrital and carbonaceous material are almost absent.

The magnesite, which is the main carbonate of this evaporite bed, forms tiny rounded granules (up to 0·01 mm. in diameter), aggregated together or disseminated through the anhydrite. Very little magnesite

is enclosed in halite. There is nothing to suggest that it is not a primary mineral. Its mode of occurrence is similar to that of the fine-grained dolomite of the other evaporite beds of this boring and to the magnesite of the Texas–New Mexico potash-field (Schaller and Henderson, 1932,

Fig. 1

Fig. 2

Fig. 1. Anhydrite-magnesite-rock with halite-anhydrite pseudomorphs after gypsum. 3838–40 feet. Natural size.

Fig. 2. Anhydrite-magnesite-rock, with halite-anhydrite pseudomorphs after gypsum. The dark matrix is rich in magnesite. 3840–42 feet. ×4.

p. 48). The relatively large hexagonal plates found in the other evaporites of this boring have not been detected in this bed. Eight refractive index measurements of magnesite from this bed give the value ω 1·700–1·702.

Anhydrite generally forms fine-grained aggregates of irregular grains, but some larger plates, often showing strain shadows, are seen to be in various stages of breakdown to form finer material. Some recrystallization of anhydrite has taken place, leading to the development of euhedral rectangular crystals. Halite areas are nearly always fringed by euhedral

elongated anhydrite crystals, and isolated crystals of anhydrite are often enclosed in halite. There has been some replacement of these crystals by halite, the anhydrite being broken up into residual pieces with common optical orientation.

Halite, pink in colour and rarely containing numerous tiny plates and rods of haematite, is present mainly as a constituent of the pseudo-

Fig. 3. Halite-anhydrite-magnesite-rock, showing replacement of anhydrite by a large crystal of quartz. 3838–40 feet. ×32.

morphs. These pseudomorphs (figs. 1, 2) are considerably smaller than most of those of the middle evaporite bed (Stewart, 1951) and are comparable with many of those found in the polyhalite zone of the lower bed (Stewart, 1950, p. 652). They reach one inch in length, are six-sided in cross-section, and often show swallow-tail twin terminations. Some consist entirely of anhydrite, but most consist of halite, with or without zones of anhydrite arranged parallel to the edges of the pseudomorphs. They are all embedded in a matrix of anhydrite and magnesite, and commonly magnesite is especially abundant at the edges of the pseudomorphs, having apparently been pushed aside as the original gypsum grew at the expense of anhydrite. More rarely, magnesitic layers pass from the matrix through the pseudomorphs, giving further evidence of the secondary nature of the gypsum.

Quartz is present in both these rocks as a subordinate constituent. It sometimes forms irregular grains surrounded by fine-grained anhydrite,

but frequently occurs as euhedral doubly-terminated prismatic crystals, which may reach 1 mm. in length. It is always euhedral towards halite, and sometimes towards anhydrite. The mineral occurs in both pseudomorphs and matrix. It frequently encloses small magnesite granules and rounded grains of anhydrite, and evidence of replacement of anhydrite by quartz is shown by the common optical orientation of corroded anhydrite relics (fig. 3).

The replacements in this zone are, then, anhydrite→gypsum→anhydrite and/or halite; anhydrite→halite; and anhydrite→quartz. Magnesite has not taken part in these replacements.

The well cuttings suggest that most of this zone consists of rocks similar to those described, but dolomite (ω 1·682) has been found in cuttings from near the base.

IV. Rocks of the zone of granular halite (with scarce rinneite).

At its base this zone gives place abruptly to the anhydritic basal zone. At its upper limit there is a fairly abrupt change in the nature of the halite, which becomes less pure and loses most of its granular texture, and this change is associated with the appearance of brown silty material. The zone can be subdivided as follows:

3790–3800 feet	Pale pink granular halite, with scarce thin layers of anhydrite. Most of the halite grains are under 1 cm. in width, but there are patches of coarse colourless or pink halite (grains up to 3 inches in width). Red sylvine has been observed in very small quantity.
3800–04	Coarse colourless halite with rinneite and sylvine.
3804–05	Granular pink halite, with coarse colourless halite, and little anhydrite.
3805–06	Coarse colourless halite with rinneite and sylvine.
3806–10	Granular pink halite, with a few thin anhydrite layers and trace of rinneite.
3810–14	Interbedded anhydrite-rich layers (up to 5 inches thick) and halite-rich layers with scarce rinneite.
3814–16	Interbedded anhydrite-rich layers, and layers of pink granular halite.
3816–24	Pink granular halite, with patches of coarse pink halite, and scarce thin layers of anhydrite. Traces of rinneite and sylvine.
3824–26	Coarse colourless halite with rinneite and sylvine.
3826–30	Pink granular halite and coarse pink to colourless halite, with scarce thin anhydritic layers and traces of rinneite.
3830–34	No samples available. The drilling log indicates that this range is largely halite.

It can be seen that most of this zone consists of halite, usually pink and granular, but occasionally colourless and very coarse. The mineral has irregular boundaries, and small liquid-filled cavities (sometimes cubic in shape) are commonly seen in thin sections. Most of the halite-rich rocks contain some anhydrite, and evidence that most of the halite has recrystallized since its formation is shown by the ejection of impurities, especially anhydrite, to form a lacy network at the edges of the halite grains. In one specimen anhydrite grains are also arranged along the halite cleavages. A few small flakes of talc have been observed, lying along the cleavages of the halite.

Contorted anhydritic layers, usually very thin, but occasionally several inches in thickness, nearly always contain tiny granules of magnesite. Much halite may be present in these layers. The anhydrite forms aggregates of small irregular grains with some larger irregular platy grains, and recrystallized elongated euhedral crystals especially where in contact with halite. There has been some replacement of anhydrite by halite. Quartz is present in small quantity in these layers, as crystals up to 1 mm. in length, and there is evidence of replacement of anhydrite by quartz. A small amount of carbonaceous material is present, but there is very little detrital material.

Sylvine occurs as small irregular bright red grains (full of haematite inclusions) associated with halite, in very small quantity. In a specimen from 3790 feet, the mineral occurs with halite in a thin layer between layers of halite and anhydrite. In some specimens rinneite occurs in this way, and it is possible that this sylvine has been derived from rinneite.

Characters and occurrence of rinneite.

Due to the exposure of the samples to the air, for several years after the boring was completed, much of the rinneite has altered to a brown mixture of halite, sylvine, and iron hydroxide. This alteration has proceeded in some cases to about one inch inwards from the surface of the core. The crust of alteration products, however, has prevented rapid decomposition of the salt, and fresh rinneite has been found in the interior of the samples. The mineral is highly deliquescent, and on exposure to air forms a brown liquid, from which sylvine and halite crystallize as small cubes. When moist material is dried in a desiccator, small deep red-brown crystals of erythrosiderite (biaxial positive, high 2V, α 1·715, β 1·751, γ approx. 1·8, strong dispersion $r>v$) form on the surface. Erythrosiderite has also been found as a constituent of the altered crust of rinneite in thin sections, and small irregular yellow

grains have been found enclosed in halite. It is unlikely that erythrosiderite was an original constituent of these rocks. Slavík (1912) has recorded the mineral as an alteration product of rinneite exposed to air.

The rinneite has the following characters: transparent and almost colourless when fresh, sometimes showing a delicate violet tint which may be due to the presence of manganese; much more brilliant lustre than halite and sylvine; very brittle; conchoidal fracture; poor prismatic cleavage; no crystal boundaries developed; H. 3; sp. gr. 2·35; does not fluoresce in ultra-violet light; readily soluble in water; taste highly astringent. The mineral is uniaxial and positive, but some sections give a biaxial interference figure with very low optic axial angle. The refractive indices for sodium-light are ω 1·588, ϵ 1·589. The dispersion is strong, and this and the low birefringence give the mineral anomalous ultra-blue interference colour in thin section and crushed fragments.

Two chemical analyses[1] of hand-picked material are given below, with analyses of material from Germany for comparison. The Eskdale analyses agree with the formula $K_3Na(Fe,Mn)Cl_6$. The analysed material from Hildesia contained 0·2 % kieserite as impurity.

Analyses of rinneite from Eskdale and Germany.

	I.	II.	Mean.	No. of cations to 6Cl.		III.	IV.
Fe	13·52	13·55	13·53	0·992	1·005	13·94	13·57
Mn	0·18	0·18	0·18	0·013		—	—
K	28·76	28·60	28·68	3·005		28·90	28·99
Na	5·71	5·62	5·66	1·008		5·61	5·69
Cl	51·94	51·94	51·94	6·000		51·87	52·02
Ca	nil	—	nil			—	—
Mg	nil	—	nil			—	0·03
SO_4	nil	—	nil			—	0·12
	100·11	99·89	99·99			100·36	100·44

I and II. Eskdale no. 2 boring, 3802·04 feet. (Analyst, E. A. Vincent.)
III. Wolkramshausen, province of Saxony. Also Br 0·04. (Boeke, 1909a.)
IV. Hildesia, Hildesheim, Hanover. Also H_2O 0·02. (Rinne and Kolb, 1911.)

[1] *Method of analysis:*

Chlorine.—Solution of salt titrated with standard silver nitrate solution, using dichlorofluorescein as adsorption indicator.

Iron.—Solution oxidized by saturating with chlorine gas, the excess of which was boiled off, and the ferric hydroxide precipitated with ammonia.

Alkalis.—Filtrate from ferric hydroxide evaporated to dryness, ammonium salts driven off, and alkalis estimated in the residue: potassium as potassium chloroplatinate, and sodium as sodium zinc uranyl acetate.

Manganese.—Estimated colorimetrically in a separate portion of the salt decomposed with strong sulphuric acid.—E. A. V.

Rinneite has been found rarely in the German salt deposits. It was first described by Boeke (1909a) from Wolkramshausen, as coarse-grained lenticular masses up to five centimetres in thickness and a few metres in length, lying parallel to the bedding of the associated halite-sylvine-anhydrite-rock. It was later described from Hildesheim (Boeke, 1909b; Schneider, 1909; Rinne and Kolb, 1911) and Salzdetfurth

Fig. 4. Halite-sylvine-rinneite-rock. Rinneite (heavily stippled) has irregular boundaries against halite (clear) and sylvine (lightly stippled). The rinneite has been partly replaced by halite and sylvine, and small rinneite relics are enclosed in both these minerals. 3802–04 feet. Natural size.

A. Vertical section of core. B. Cross section of core.

(Boeke 1911) associated with kieserite, halite, and sylvine; from Riedel (Rinne and Kolb, 1911) in small quantities in halite-sylvine-rock; and from Hope (Harbort, 1928) associated with halite, anhydrite, zirklerite, quartz, dolomite, and clay. The mineral has also been recorded as a sublimation product at Vesuvius (Zambonini and Restaino, 1925; Zambonini, 1931) and the crystal structure of artificial material and of material from this locality has been worked out by Bellanca (1948).

In the Yorkshire potash-field the mineral occurs in these upper evaporites in the Eskdale no. 2 boring (Stewart, 1949), and has been found by the Geological Survey in the marls between the upper and middle evaporites in the recent I.C.I. borings (Fleck, 1950). Rinneite from these marls in Fisons's boring at Robin Hood's Bay has been exhibited to the Geological Society by Hollingworth and Stewart (1950). There it is undoubtedly of secondary formation, being associated with halite, sylvine, and carnallite, filling cracks in the marls.

In the zone of granular halite of the Eskdale no. 2 evaporites, the mineral occurs in some abundance in samples from 3800–04, 3805, and 3824–26 feet. These are coarse halite-sylvine-rinneite-rocks, with very

scarce anhydrite (figs. 4, 5B). Analyses show 3·22 % KCl at 3800–02 feet; 6·66 % KCl at 3824–26 feet. The halite forms colourless irregular grains up to three inches in width. In slice, it contains abundant elongated liquid-filled cavities, arranged in many cases along dodecahedral planes. The lines of inclusions are sometimes curved, and the individual inclu-

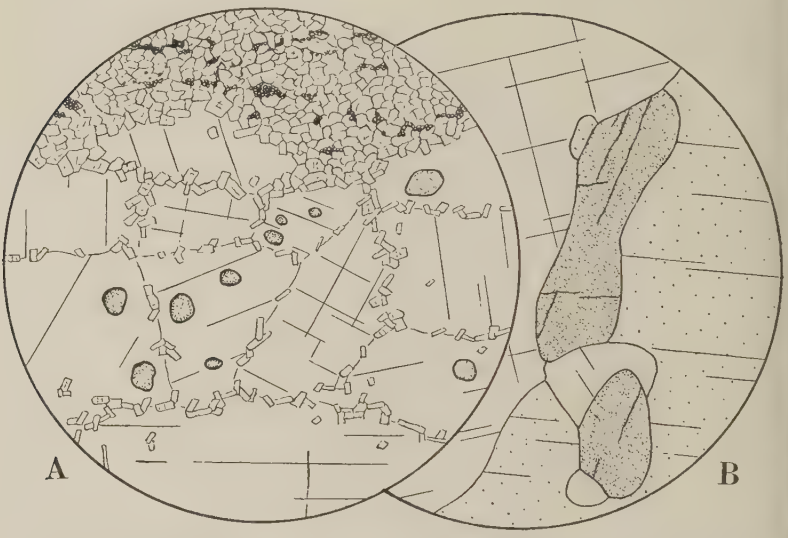

FIG. 5A. Halite-anhydrite-rinneite-rock, with (at the top) part of a layer of anhydrite-magnesite-rock. Rinneite (stippled) forms rounded relics, all having the same optical orientation. The distribution of anhydrite grains between halite grains suggests that this anhydrite has formed during or after replacement of a large rinneite grain by halite. 3810–12 feet. ×12.

FIG. 5B. Halite-sylvine-rinneite-rock. Two rounded relics of rinneite (heavily stippled) have common optical orientation, and the same orientation as larger grains outside the field of view. Rinneite has been replaced by sylvine (lightly stippled) and halite. 3802–04 feet. ×8.

sions streaked out and curved in common directions, giving evidence of movement of halite under strain. The halite cleavages are, however, regular and straight, showing that the halite has recrystallized after it was distorted. Sylvine occurs in these rocks as irregular milky-white grains, free from haematite inclusions, and reaching one inch in width. The sylvine grains contain many tiny rounded inclusions of halite. Rinneite forms patches rarely reaching 2 inches in width, with very irregular boundaries against halite and sylvine. In many cases these patches consist of a single large grain of rinneite; in other cases they

consist of coarse-grained aggregates. The intricate nature of the margins suggests replacement of rinneite by both halite and sylvine, and this is borne out by the occurrence of small rounded relics of rinneite, in the same optical orientation as adjacent larger patches, enclosed in both halite and sylvine. In such a replacement $FeCl_2$ must have been removed in solution. The lack of displacement of the rinneite relics would indicate that the replacement took place at a late stage, after movement of the halite under the load of the overlying rocks.

Many other specimens from this zone show small quantities of rinneite, as rounded grains associated with halite. In two specimens (3810–12, 3812–14 feet) the mineral occurs with halite in layers up to a centimetre in thickness, between anhydritic and halite-rich layers. Although we do not know which was the upper side of the specimens, it seems likely that the succession from base to top is anhydrite-magnesite-halite-rock, halite-anhydrite-rock, halite-anhydrite-rinneite-rock. The specimens consist of a repeated series of these units. In these rocks, again, there is definite evidence of replacement of rinneite by halite. Small relics of rinneite, enclosed in halite, have common optical orientation over wide areas in thin section, so that the original rinneite must have occurred as large grains (fig. 5A).

The occurrence of rinneite in the layered series described above suggests that it may have been a primary mineral. There is no evidence that it has replaced any other mineral. However, the late recrystallization in these rocks would tend to destroy evidence of early replacements.

V. Rocks of the zone of silty halite.

The main divisions of this zone have been shown above in the table of the general succession, and it has been mentioned that the upper part of the zone was not cored. The minerals found are halite, sylvine, carnallite, anhydrite, magnesite, haematite, quartz, and talc. All these minerals may occur in the same rock. In addition, very small quantities of an unidentified green, highly deliquescent mineral, containing ferrous and potassium chloride, have been found as inclusions in halite.

There is a considerable quantity of brown silty material in many specimens, sometimes forming irregular layers, but normally occurring as patches between halite grains. This material consists largely of angular grains of quartz, with chloritic and clay material, a few flakes of muscovite, and haematite. Crystals of anhydrite and euhedral quartz

are found in the silt patches, and these patches are impregnated with halite, and often veined by halite, anhydrite, and quartz. Silt is particularly abundant in the depth ranges 3738–56 and 3768–82 feet.

Halite varies from colourless to pink and reddish-brown, and is very variable in grain-size, the grains sometimes being as much as two inches across. Haematite inclusions in halite are relatively rare. The concentration of impurities in interstitial patches and the distortion of anhydritic and silty patches indicate that the halite has suffered widespread recrystallization. Sylvine is very scarce and occurs as small pink or red grains, full of haematite inclusions, associated with halite. Carnallite (α 1·467, β 1·475, γ 1·498, sodium-light) occurs in most specimens in very small amount, as irregular pink grains up to a few millimetres in diameter, associated with halite. These grains are free from haematite inclusions, and sometimes contain many small elongated euhedral crystals of anhydrite. No replacement involving carnallite or sylvine has been noted.

In the lower rocks of this range anhydrite occurs as thin contorted layers and patches, pink or brown in colour due to admixture with silty material. In the upper rocks anhydrite is not so abundant, and forms small patches, and isolated crystals enclosed in halite or associated with silt. The veining of silt patches by anhydrite shows that there has been some redistribution of this mineral. Beautiful examples of large recrystallized euhedral anhydrite plates enclosed in a very fine-grained anhydrite matrix are seen in several slices (fig. 6B). There has been some replacement of anhydrite by halite and by quartz.

Magnesite is very scarce, and only a few small grains have been observed. Haematite occurs as tiny hexagonal plates and rods enclosed in sylvine and rarely in halite, and is an abundant constituent of the silt patches.

Quartz is extraordinarily abundant, even more abundant than in the halite zone of the middle evaporite bed. Non-detrital quartz forms over 5 % of some slices. Euhedral crystals are found in large quantity projecting into halite from the edges of silt patches, and occur in smaller quantity as isolated crystals enclosed in halite, and in layers and patches of anhydrite. They frequently enclose detrital quartz grains, but have not normally grown in optical continuity with these. Quartz crystals enclosed in halite have been seen to contain a rectangular network of talc plates, lying parallel to the talc which lies along the cleavages of the enclosing halite. This indicates replacement of halite by quartz, after the formation of secondary talc (fig. 6A).

A few flakes of talc can be detected in most specimens, and this mineral becomes very conspicuous in the range 3763–82 feet. It occurs as very thin silvery plates, with irregular outline, up to a few millimetres across. Its characters are similar to those of the talc of the lower evaporite bed, and refractive index measurements give α 1·540, $\beta = \gamma$ 1·587. As in the lower evaporite bed, it is invariably associated

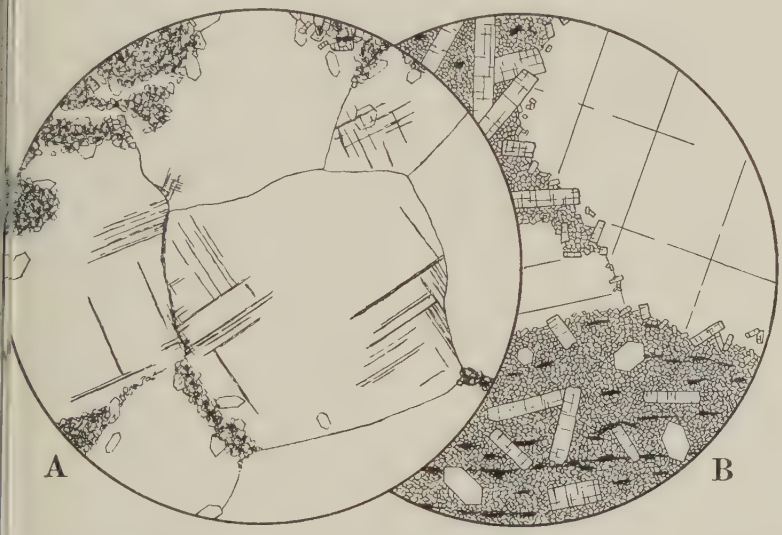

Fig. 6a. Halite-talc-quartz-rock, with some anhydrite, and patches of clastic material full of angular quartz grains. Talc plates lie along cleavages and intergranular boundaries of halite. Halite cleavages are not shown in this diagram except where talc is present. Euhedral quartz is abundant, and in the upper right quadrant talc plates pass through a quartz crystal, indicating replacement of halite by quartz after the formation of talc. 3780–82 feet. ×12.

Fig. 6b. Halite-anhydrite-quartz-rock, with elongated patches of clastic material. Patches of fine-grained anhydrite contain euhedral quartz and anhydrite porphyroblasts. 3782–84 feet. ×12.

with halite, and forms rectangular networks of plates lying along the halite cleavages. Intergranular boundaries between halite grains are sometimes lined with talc, and plates pass from these boundaries along the cleavages of the adjacent halite. It would appear that it is a secondary mineral (Stewart, 1949, pp. 665–669). Talc has recently been recorded from the potash-field of New Mexico, where it is considered to be secondary (Bailey, 1949).

VI. Summary and conclusions.

The evaporite bed is 205 feet thick, and has been divided into three main zones; a basal anhydrite-rich zone; followed upwards by a zone of granular halite, with subordinate anhydrite and rinneite; and then a zone of silty halite, with subordinate anhydrite and a considerable quantity of clastic material.

Recent I.C.I. borings (Fleck, 1950) have proved a sylvine-halite zone in the upper evaporites of this potash-field. No such zone has been found in the rocks described here, but since the upper 80 feet of these evaporites was not cored it is possible that such a zone exists in that range. However, consideration of the sections published by Fleck suggests that this zone should lie above the granular halite zone with its rinneite-bearing rocks, but not far above this zone, and it seems quite possible that the sylvine-halite zone does not exist at this locality.

The following minerals have been found: anhydrite, carnallite, dolomite, haematite, halite, magnesite, quartz, rinneite, sylvine, and talc. The major constituents are halite, anhydrite, and magnesite. Quartz is even more abundant than in the middle evaporite bed. Talc is widespread in the zone of silty halite and is believed to be a secondary mineral. Rinneite is found over a range of 30 feet, and there is no evidence that it has replaced any other mineral. Early gypsum is represented by anhydrite-halite pseudomorphs in the basal zone. Quartz, magnesite, and potassium salts make an appearance, and dolomite disappears, much earlier in the succession than in the middle evaporite bed.

There has been widespread recrystallization of halite and anhydrite. There is evidence of the following replacements: anhydrite → gypsum → anhydrite and/or halite; anhydrite → halite; anhydrite → quartz; halite → quartz; rinneite → halite; rinneite → sylvine. The replacements involving gypsum are thought to have taken place at an early stage, during the deposition of the evaporites. If, as is thought probable, most of the halite has recrystallized under load, the other replacements may be late ones, since recrystallization of halite would tend to obscure the microscopic evidence of early replacements.

This paper concludes the petrological study of the evaporites of the Eskdale no. 2 boring. It may be said in general conclusion that the study has shown that each of the evaporite beds has its own distinctive characters. The evaporites from this locality show many features not as yet recorded from the outlying parts of the salt-field; in addition to

the potassium salts and their associates, the occurrence of magnesite and quartz as important constituents is striking. Talc has not been recorded from the outlying districts, but I have seen this mineral in cores from the I.C.I. borings in the Guisborough-Redcar district. I have also seen abundant pseudomorphs of anhydrite after gypsum in a specimen from the D'Arcy Exploration Company's boring at Hayton, and these pseudomorphous rocks should be looked for in other parts of the salt-field. Although the British and German deposits show many features in common, there are also striking differences; the abundance of quartz, the presence of talc, and the relative scarcity of magnesium-bearing minerals in the chloride zones, are obvious examples. The recent borings should provide interesting data on the lateral and vertical distribution of the accessory minerals of these deposits and on the nature and extent of the replacements recorded, and will give much scope for research on the problems of salt petrology.

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Some physical properties of raw and calcined flint.

(With Plate XIV.)

By J. H. Weymouth, B.Sc.
and W. O. Williamson, B.Sc., Ph.D., A.R.I.C.

Division of Industrial Chemistry, Commonwealth Scientific and Industrial Research Organization, Australia.

[Read by Dr. G. F. Claringbull, March 8, 1951.]

Introduction.

FLINT from the chalk of north-western Europe has long been an ingredient of ceramic 'bodies'. It is still widely used by British pottery manufacturers in glazed tiles and in certain types of tableware. Continental manufacturers also have made some use of it.

Flint is more readily converted to cristobalite than are the coarser-grained varieties of quartzose silica. The presence of an adequate amount of cristobalite in the 'body' ensures that, at room-temperature, the glaze-film on the ware shall be under a compressive stress. Thus the development of 'crazing', i.e. of minute tension-fissures in the glaze, tends to be avoided. The compressive stress arises because, during the cooling of the glazed ware in the kiln, the diminution of volume which accompanies the change high-cristobalite → low-cristobalite produces an accelerated thermal contraction of the body. This temporarily accelerated contraction puts the more slowly shrinking glaze under compression and the resulting strain is not easily released at the low temperatures involved (Webb, 1939; Simpson and Webb, 1939).

Before flint is added to a pottery body it is calcined. Calcination serves essentially to make the flint easier to grind and, incidentally, to change the colour of the flint from black or greyish-black by incident light to white. The industrial calcination of flint has been practised for over two centuries, but only since 1900 have acceptable explanations been advanced of the more obvious phenomena which accompany it. Certain phenomena are still neglected or only inadequately explained. It is hoped in the present contribution to extend our knowledge of them.

The nature of flint.

It is probable that flint and other forms of chalcedonic silica are essentially cryptocrystalline quartz. Imperfection or distortion of the quartz lattice (Shishacow, 1936) may cause certain properties of these minerals to differ from those of more coarsely crystallized quartz. Correns and Nagelschmidt (1933) have, however, explained the peculiar optical properties of chalcedony by considering the arrangement and crystallographic orientation of the quartz fibres of which, according to their X-ray studies, it is composed. X-ray investigation by A. W. Hull (see Washburn and Navias, 1922) has proved that both chalcedony and European flint contain considerable amounts of quartz.

Thermal expansion curves have demonstrated the existence of the low-quartz $\rightleftarrows$ high-quartz transition in flint (Houldsworth and Cobb, 1922; Holdridge, Nancarrow, and Francis, 1942), and in chalcedony (Le Chatelier, 1914). Thermal analysis, however, has not always produced evidence of this transition in chalcedony and flint (Fenner, 1913, but cf. Sosman, 1927, p. 177; Pressler and Shearer, 1926; White, 1927) or in chert (Tuttle, 1949): despite the negative result for chert, X-ray photography showed quartz to be present therein.

H. V. Thompson made two analyses of European flint for Mellor and Campbell (1916) in which slightly over 1 % of water was reported; our own figure is similar. Holdridge et al. (1942) suggested that the water might be present as a monomolecular film binding together aggregates of silica molecules. Their hypothesis, though over-simplified, was significant because it implied an adsorption of water by the flint material as a whole. Alternatively, water may be regarded as associated more particularly with the opal which has been reported by some investigators. Tarr (1926) and Bosazza (1937) identified opal in English flint microscopically; indeed, Bosazza reported 76 % of it in a water-ground sample. Such material is invariably calcined prior to grinding and identification of opal therein must be discredited.

The heating of flint with caustic soda solutions causes preferential attack (cf. Oakley, 1939). This attack is not specifically on opal because fine-grained quartz is appreciably affected (cf. Correns and Nagelschmidt, 1933).

The presence of well-distributed opal could explain the fact that the density and refractive index of chalcedony or flint are both less than those of quartz. The hypothesis of a minute porosity is an acceptable alternative (see below); adsorbed water also could influence the two properties cited.

Some reported effects of heat on flint and chalcedony.

Density.—Mellor and Campbell (1916) showed that the density of flint decreased to 2·22 after repeated calcinations at temperatures of presumably between 1250° and 1300° C. The range of densities listed for cristobalite by Sosman (1927, p. 303) is 2·310–2·320. Rieke (see Robson, 1922), Hirsch (see Simpson and Webb, 1939), and Holdridge et al. (1942) also obtained anomalously low densities for calcined flint. The same was true of Washburn and Navias (1922) whose very careful determinations gave: $d_{25°}^{25°}$ 2·251 for flint which had been heated for 4 hours at 1430–1460° C. Chalcedony similarly treated gave $d_{25°}^{25°}$ 2·175. Calcined chalcedony had frequently been described as having a peculiarly low density although dilatometric evidence suggested that it was cristobalite (cf. Endell and Rieke, 1913, and refs. there cit.; Le Chatelier, 1890, 1914).

Houldsworth and Cobb (1922) recorded the presence of cristobalite in calcined flint and based their conclusion on both dilatometry and refractive index measurement; they made the novel claim that tridymite appeared in some circumstances (cf. Sosman, 1927, p. 85).

A distinct advance in our knowledge was made when Hull demonstrated to Washburn and Navias (1922) by X-ray powder photography that cristobalite was the only crystalline phase detectable in strongly calcined flint or chalcedony.

The apparently low densities of calcined cryptocrystalline silica may depend on the existence in its structure of fine cracks or pores not readily accessible to a liquid (Endell and Rieke, 1913; Le Chatelier, 1914). Washburn and Navias (1922) showed that when calcined chalcedony was very finely ground its measured density increased by 2 %. This result was thought by the investigators to indicate the presence of many minute pores. The interpretation is well founded, for the density of very finely ground quartz normally appears to be greater, not less, than that of coarser material. This phenomenon has been attributed to the formation of amorphous silica (e.g. by Martin, 1927), but adsorption effects, involving the liquid used in the determinations of density, provide complicating factors (Culbertson and Weber, 1938).

Simpson and Webb (1939) assumed the existence of micro-capillary air spaces, impenetrable by liquids, between the quartz fibres of calcined flint. Heating induced a thrust of the fibres and an escape of water which tended to increase the number of these spaces. Thus the density of the flint appeared to fall before there was any conversion to cristobalite, and the cristobalite which finally appeared was itself of

anomalously low density (cf. Sosman, 1927, pp. 273 and 388; Holdridge et al., 1942).

There is thus general agreement among investigators that the measured densities of calcined flint or chalcedony are affected in some degree by the presence of minute pores inaccessible to liquids. Other suggestions have been made, but on slender evidence. Sosman (1927, p. 273) mentioned the possibility that the fall in density of cryptocrystalline silica, which supervenes at low temperatures, might depend on some rearrangement of molecules to give a cristobalite-type of structure. This rearrangement was promoted by the water present in such silica and ceased when it had been evolved. There is, indeed, experimental evidence that water may promote the formation of cristobalite, but here the initial silica was amorphous (Cohn and Kolthoff, 1948). Washburn and Navias (1922) thought that states intermediate in crystallinity, and thus in density, between those represented by silica-glass and by eucrystalline cristobalite might be possible. This idea receives some support from the claim of Endell (1948) that appropriate thermal treatment of kieselguhr produced a material of a degree of crystallinity intermediate between that represented in amorphous silica and in low-cristobalite; X-ray evidence was used to support this thesis.

Refractive index.—Flint is known to show a decreased refractive index after calcination, but no systematic study of the phenomenon has yet been published. Washburn and Navias (1922) and Williamson (1941) found that the refractive indices, determined by immersion, of some samples of calcined flint were distinctly above the values for the mean refractive indices of low-cristobalite or low-tridymite tabulated by Sosman (1927, pp. 599–600), but below those of quartz. Sosman (1927, p. 273) was aware that the refractive index of calcined cryptocrystalline silica could be affected by the presence of pores. Ostwald (1924) and Dunham, Claringbull, and Bannister (1948) have mentioned comparable phenomena.

Colour.—The flints used in the European ceramic industries are frequently obtained from sea-beaches as pebbles or boulders; sometimes they are taken directly from the chalk. The British potter has been wont to recognize two types of flint among the material from beaches, namely 'black' and 'grey'. Grey flints are said to shatter more readily than black flints during calcination (Mellor and Campbell, 1916; Heath and Leese, 1923). The essential differences, if any, between the two types remain undetermined.

Raw flint is predominantly black or greyish-black unless it has been stained or altered. Some investigators have agreed that carbonaceous matter contributes to the production of the colour or is even its sole cause (cf. Tarr, 1926; Washburn and Navias, 1922). Alternatively the finely particulate structure of the rock may be assumed to prevent most of the incident light from being reflected to the eye (Tarr, 1926; Oakley, 1939). Indeed, if a minutely fibrous structure be ascribed to the chalcedony in the flint, an effect may be expected comparable to the dark appearance of needle-points bunched closely together and facing the observer (cf. Woods, 1934, p. 106, for a discussion of this and similar optical phenomena).

Adequate calcination of flint causes it to become white by incident, though not by transmitted, light. This whitening may not depend entirely on the oxidation of carbonaceous matter, for it can be ascribed also to reflection from the planes along which the flint has fractured during heating (Oakley, 1939; Holdridge et al., 1942).

Calcined flint, although white by incident light, shows an unexplained brownish colour by transmitted light even in sections only 30–40 microns thick (Williamson, 1941, 1949). The existence of this brownish colour can be inferred from photomicrographs of partially fused fels-par-flint mixtures provided by Heath and Mellor (1914), and of flint serving as a constituent of silica-bricks (Hugill and Rees, 1931). None of these authors comments on the colour. The classical paper by Klein (1916) on the micro-structure of porcelain suggests that he was deceived by the brownish colour of the flint in an English tableware body into confusing flint with calcined clay.

The flint of the present experiments.

This flint was in the form of boulders obtained, through commercial sources, from English sea-beaches. It was of the type termed 'grey' by potters. When examined microscopically, it was found to have a fine-grained siliceous matrix in which there were many coarser areas of calcareous or siliceous material. A few of these areas were manifestly sections of organic structures, but it is likely that many of them occupied the sites of former structures of this kind. Obvious also were numerous separate or aggregated thin annuli of chalcedony which gave the initial impression of having replaced the shells of foraminifera. Most, or all, of them were probably of inorganic origin. Some of these annuli enclosed a brownish material, existing also in a few irregular areas outside them, which showed an aggregate polarization like that of the matrix. There

was no good reason for identifying the material as opal rather than as chalcedony; indeed, no satisfactory examples of opal were encountered. Further, no opal was obtained by centrifuging finely powdered flint with liquids of appropriate density.

Only a single specimen could be confidently recognized as a foraminifer. The more interior parts of its shell were still calcareous but the remainder had been replaced by chalcedony. This mineral had commonly developed as negatively elongated fibres traversing the thickness of the shell (pl. XIV, fig. 1). Similar processes of silicification had affected other structures, elsewhere in the flints, identified as fragments of lamellibranch (or brachiopod) shells. Usually replacement had been by fibres of chalcedony arranged in the manner just described, but occasionally by a mosaic of chalcedony grains without obvious structure. A few radiolaria were noticed and there were some fragments which appeared to be sponge remains.

Sporadic spherulites of chalcedony had diameters up to 0·2 mm. Related bodies were apparent in which elongation sometimes sufficed to produce rectangular or tapering areas in which parallel fibres sprang from both sides of the central axis (pl. XIV, fig. 2). Some of these rectangular structures may have been sponge spicules. It is, of course, possible that certain 'spherulites' are merely cross-sections of the rectangular structures. Fan-like growths of chalcedony were common and some formed aggregates. In certain aggregates the fibres diverged from points on the boundary between the aggregate and the fine-grained matrix which surrounded it (pl. XIV, fig. 3). This arrangement suggests growth into a cavity which initially was empty or, more probably, occupied by calcareous material presumably of organic origin. A rare type of spherulite had a wide core of radiating chalcedony fibres and a discontinuous outer shell of calcitic material into which the spherulitic structure sometimes continued.

The fine-grained matrix of the flint was not a mosaic of equi-dimensional grains. High magnifications revealed it as crenulated or interlocked units grading downwards in size until they were no longer distinguishable. Each unit showed undulose extinction of a type which suggested the presence of minute fibres with a fan-wise disposition. In the coarser units such a structure was actually detectable. Indeed, there was a gradation in size between the units of the matrix and the coarser chalcedonic structures already described.

Chalcedony fibres of all lengths and arrangements had the usual negative elongation; positive elongation was rarely found.

Certain regions of extensive silicification appeared to occupy the sites of coherent sponge remains and in some of these regions were seen collections of granules which were probably carbonaceous.

The flint matrix contained rhombohedral carbonate as specks or as small crenulate units interlocked with the silica. The distribution of this fine calcitic material was not uniform and was unrelated to that of the larger patches of carbonate; a few of these patches were clearly the remains of fossils.

One section contained an interesting inclusion (pl. XIV, fig. 4). This appeared as a crudely rectangular area with approximately parallel longer sides and irregular ends. Its dimensions were about $2{\cdot}5 \times 1{\cdot}5$ mm. It contained a broad axial belt of contiguous crystals of carbonate which were dominantly hexagonal in outline. This belt was flanked on both sides by zones of silica. The silica consisted of quartz units which had replaced the euhedra of carbonate and had usually preserved their shape. Sometimes a discrete quartz crystal had replaced a particular euhedron of carbonate; some pseudomorphs, however, consisted of several quartz crystals. Mechanical extraction yielded sufficient carbonate for spectrographic examination. The carbonate was distinctly ferriferous and had some Mg and Ca, with traces of Na and P. The process of silicification to which it had been subjected would appear to be that which affected also the more obviously organic structures, still partially preserved in calcareous material, seen elsewhere in the sections.

Wells (1947) described the replacement by silica of carbonate rhombs contained in chert. Further, he directed attention to occurrences of rhomb-bearing cherts in limestones free from rhombs. The association of a rhomb-bearing flint with the chalk would resemble such occurrences. However, the aggregated euhedra first described may well be a section cut from the prismatic layer of a large lamellibranch (or brachiopod) shell. The rhombs discussed by Wells appear to have been of inorganic origin.

The mean refractive index of the siliceous material of the flint matrix was 1·538 for sodium-light; the corresponding density was 2·622. These figures are below those commonly recorded for quartz, although only quartz was identified in the sample by X-ray powder photography. If opal were present it was in an amount too small to show the X-ray diffraction effects to be expected from a silica gel. Much of the quartz was, however, very fine-grained. Further, thermal expansion curves, obtained from test pieces made of crushed flint bonded with a little

bentonite, revealed the volume change which accompanies the low-quartz $\rightleftarrows$ high-quartz transition.

Cristobalite, if present, was in an amount too small to be detected by the X-ray powder photographs. This possibility was considered because low- or high-cristobalite has been reported in association with opal (Greig, 1932; Levin and Ott, 1933).

An analysis of the raw flint is shown in table I. The preponderance of Na_2O over K_2O is found also in other analyses of flints from sea-beaches (Mellor and Campbell, 1916; Holdridge et al., 1942). Consequently it may indicate something other than vagaries of analytical technique. Exchange or other reactions, or adsorption effects, involving sea-water may be responsible for it. The trace of chloride also suggests interaction with sea-water.

TABLE I. Analysis of raw flint. (Analyst, Miss B. C. Terrell.)

SiO_2	...	98·19	H_2O-	...	0·33
Al_2O_3	...	nil	CO_2	...	0·24
*Fe_2O_3	...	0·02	TiO_2	...	nil
MgO	...	0·21	P_2O_5	...	0·03
CaO	...	0·30	Cl	...	trace
Na_2O	...	0·08	SO_3	...	nil
K_2O	...	0·03			
H_2O+	...	1·11			
					100·54

* State of oxidation not determined.

The loss in weight of flint on ignition is caused almost entirely by the evolution of water and the decomposition of carbonates. Water tends to be expelled at lower, and carbon dioxide at higher, temperatures. An investigation was made by using an apparatus devised by Mr. A. J. Gaskin. This apparatus plots automatically a continuous isobaric curve of weight-loss against temperature. It is designed in such a way that the sample is maintained in an approximate equilibrium over the whole temperature range; a determination occupies some 50 hours. The resulting curve for flint is shown in text-fig. 1. The pronounced upward inflection between 300° and 400° C. accords with the marked loss in weight found at 350° C. by Holdridge et al. (1942). These investigators used a technique differing from that here described and the two sets of results are not quantitatively comparable. The sudden inflection between 600° and 700° C. can be ascribed to the loss of CO_2 from carbonates.

Experimental.

Density.—To avoid the extensive contamination likely to accompany the fine-grinding of the tough flint, the material was broken merely into chips prior to calcination. These chips were $\frac{1}{2}$–$\frac{3}{4}$ inch long and their greatest thickness did not exceed $\frac{1}{4}$ inch. The calcined flint was readily friable, except when it had been produced at temperatures below 900° C. It was pulverized in an alumina mortar.

In preliminary experiments the flint was heated for 9 and for 18 hours at some of the lower calcination temperatures to be employed. As the longer period of heating caused little or no further reduction in density the standard time of 9 hours calcination was adopted, but it is not claimed that the densities reported are equilibrium values.

Calcination was performed in electrical resistance furnaces equipped with temperature-controlling mechanisms and recording pyrometers. It was, however, necessary to employ a gas-fired pot furnace for the highest temperature attained. Here the atmosphere was distinctly reducing. The temperature in this furnace was determined by an optical pyrometer and was somewhat above 1500° C.; a more accurate estimate was not practicable.

The calcined material was ground to pass a 200-mesh B.S. sieve and its density was determined in water at 25° C. by the use of a pyknometer. Despite the addition to the water of a small amount of a wetting agent, it was noticed that any ultra-fine material produced in grinding floated persistently. Although the production of such material was minimized as far as possible, it was necessary to remove the material by washing. We are aware that Washburn and Navias (1922) recorded that the density of very finely ground calcined flint was 2 % greater than that of coarser material. However, our measured values are in any case only the average given by mixtures of particles of slightly differing densities. This follows from the somewhat varied thermal behaviour to be expected from parts of the flint which differ in degree of crystalline perfection or development, e.g. the coarser spherulitic and other structures and the fine-grained matrix. The existence of such a phenomenon was confirmed by suspending samples of powdered calcined flint in liquid diffusion columns; most particles had similar densities, but a few had slightly aberrant densities. It can be accepted, however, that the densities measured pyknometrically are dependent chiefly on the thermal behaviour of the material termed 'matrix' in the microscopical description (see above) as this material predominates in the flints.

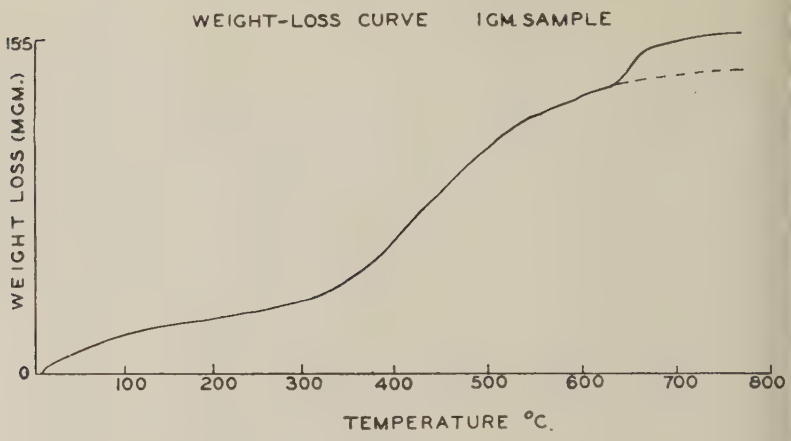

Fig. 1. Weight-loss versus temperature curve for flint. A 1 gm. sample lost a total of 15·5 mgm.

Table II. Effect of calcination on some properties of flint.

Calcination temperature.	Density.	Porosity (Calculated).	Refractive index Found.	Calc.	Phases identified by X-rays.
Uncalcined	2·622	1·03 %	1·538	1·543	quartz
200° C.	2·612	1·42	1·536	1·541	—
300	2·611	1·44	1·534	1·541	—
400	2·593	2·12	1·530	1·538	—
500	2·553	3·64	1·520	1·529	—
600	2·499	5·66	1·515	1·519	—
700	2·493	5·90	1·514	1·516	—
800	2·490	6·01	1·512	1·516	—
900	2·485	6·17	1·512	1·515	quartz
1000	2·489	6·03	1·512	1·515	quartz
1050	2·495	5·81	1·511	1·517	—
1100	2·506	5·42	1·510	1·519	quartz
1200	2·472	6·67	1·508	1·512	quartz + some cristobalite
1300	2·268	2·21	1·476	1·474	—
1400	2·224	4·08	1·469	1·465	cristobalite
1400° C. (recrystd. 1000° C. Na_2CO_3)	2·283	1·55	1·479	1·478	cristobalite
1400° C. (recrystd. 1500° C.+)	2·319	nil	1·485	—	cristobalite

The results are summarized in table II and fig. 2. A decrease in density begins at the lowest temperatures of calcination and becomes

more pronounced at 300° C. At this latter temperature the dehydration curve (fig. 1) displays an upward trend. The decrease in density continues to 600° C.; a flattening of the dehydration curve has already become apparent somewhat below this temperature. This flattening is

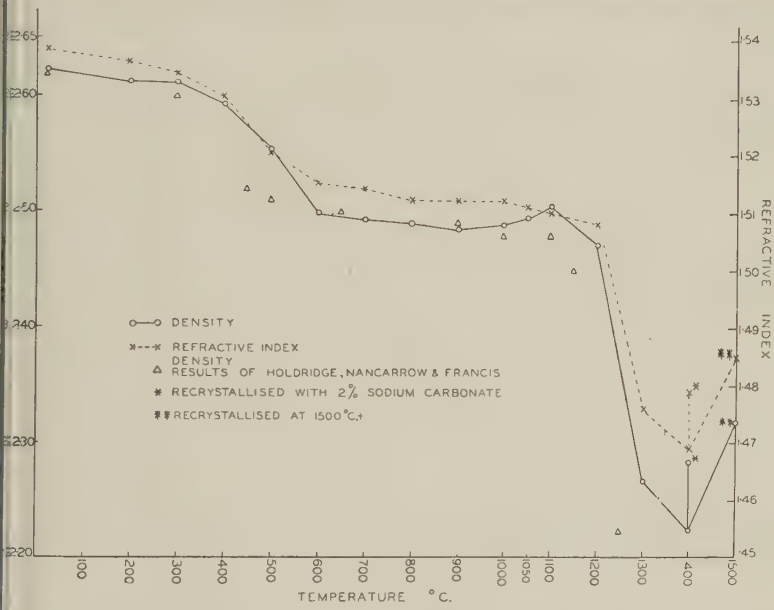

Fig. 2. Density/temperature and refractive index/temperature curves for flint.

now continued in sympathy with the near-horizontal portion of the density curve, and is seen particularly in the extrapolated portion of the dehydration curve (represented in fig. 1 by a broken line). The sharp upward inflection in the weight-loss curve between 600° and 700° C. can be ignored because it was produced by the loss of CO_2 from carbonates.

The density curve tends to be horizontal between 600° and 1000° C. A slight upward trend then supervenes and continues to 1100° C. From this temperature the decrease in density, now marking the formation of cristobalite, becomes very noticeable. Cristobalite was first detected in material calcined at 1200° C.; this temperature is close to the 1150° C. determined by Holdridge et al. (1942). Hitherto, despite apparent changes in density, the flint has consisted entirely or predominantly of quartz.

The temperature-density curve agrees approximately in shape with

the generalized curve depicted by Simpson and Webb (1939), but its initial descent ceases at 600° C., not 300° C., and the later descent, accompanying the formation of cristobalite, begins at 1100° C., not about 950° C.

The reason for the slight rise in density between 1000° and 1100° C. has not yet been elucidated; indeed, elucidation is likely to prove difficult. Factors which could promote an increase in density include one or both of the following:

(*a*) A sintering or other process which, without forming a new phase, produced a more compact structure.

(*b*) The formation of quartz from amorphous material in the flint.

Schulman, Claffy, and Ginther (1949), and Bailey (1949) showed that amorphous silica or silicic acid were converted to quartz in the presence of lime. Not only does flint contain lime, but the increased density appears at temperatures where these investigators found that quartz was effectively produced.

At 1400° C. the flint, though now converted to cristobalite, has a density considerably below that quoted for this material. The phenomenon presumably results from the persistence of minute pores. Attempts were therefore made to increase the density by recrystallization. Two methods were used:

(1) The material was reheated with 2 % of sodium carbonate for 9 hours at 1000° C. This caused a distinct increase in density. The resulting solid was still cristobalite.

(2) The material was reheated for 6 hours at temperatures somewhat greater than 1500° C. The product was cristobalite of normal density (table II; fig. 2).

The density figures obtained by Holdridge et al. (1942) have been plotted with ours in fig. 2. There is a considerable measure of accord along the near-horizontal portion of the curve. Presumably the structure of calcined flint attains a certain stability at about 600° C. and maintains it throughout the temperature range represented by this portion of the curve. In regions where drastic structural changes are occurring, i.e. below 600° and above 1000° C., the densities obtained by various investigators may well be expected to differ.

Refractive index.—The material which had been used to study the effect of heat-treatment on density was employed also for determinations of refractive index in sodium-light by immersion technique. The fact that a scatter of density values had been found in individual samples

led naturally to the supposition that a scatter of refractive indices would be found also. This was, in fact, true; commonly there were some grains of refractive index slightly higher than that of the mass of the material. Presumably the more robust structural units in the flint are apt to maintain rather higher densities or refractive indices than does the fine-grained matrix when both receive the same thermal treatment. Differences in density or refractive index within the same sample tended to diminish as the temperature of calcination increased and to be annulled where there had been an extensive development of cristobalite. Further, the grains commonly showed an aggregate polarization in shades of grey which was marked in the quartz-containing specimens. However, the mean refractive indices of that part of the flint previously termed the 'matrix' were determined and showed a remarkable correlation with the corresponding densities (fig. 2).

An anomalously low refractive index may be exhibited by material which is still quartz and not cristobalite; this effect can be ascribed to the presence of minute pores. The peculiarly low refractive index of the cristobalite prepared from flint at 1400° C. is similarly explicable.

Recrystallization of the cristobalite to give a less porous structure should be accompanied, not only by the rise in density which has already been demonstrated, but by a rise in refractive index. The data in table II and fig. 2 show that this is so. In particular, the recrystallization of cristobalite at temperatures slightly greater than 1500° C. yielded a product not only with a normal density but with a normal refractive index (cf. values listed by Sosman, 1927, p. 599). Some results described by Robson (1922) appear to be comparable; he reheated industrially calcined flint at temperatures which were probably about 1400° C. and obtained a product with the refractive index of cristobalite.

Ostwald (1924) cited investigations which showed that the measured refractive indices of hydrophane or of tabashir depended on the particular liquid with which these materials were soaked. In calcined flint the pores are filled, not by liquid, but by gas (presumably air, water-vapour, and carbon dioxide, although some pores may be empty), but a similar phenomenon arises. In contrast to the behaviour of hydrophane or tabashir, it is not possible to replace any substantial proportion of the contained gas by a liquid.

Some of the investigators cited by Ostwald showed further that an approximation to the measured apparent refractive index of soaked siliceous material can be calculated by using an appropriate mixture-

formula involving the refractive index of the solid silica and of the soaking liquid.

A similar calculation for flint has been made on the basis of the following assumptions:

(1) The raw flint consists of quartz.
(2) Flint calcined up to and including 1200° C. is exclusively quartz.
(3) Samples calcined above 1200° C. are exclusively cristobalite.
(4) The density of quartz is 2·649 and its mean refractive index is 1·549.
(5) The density and refractive index of cristobalite are those recorded for the sample recrystallized at temperatures somewhat greater than 1500° C. (table II).

The porosities and refractive indices of the samples were calculated from the formulae:

$$P = 100\left(1 - \frac{Da}{Dt}\right) \quad \text{and} \quad N = \frac{Vs.Ns + Vp.Np}{Vs + Vp},$$

where P is the percentage true porosity of the solid, Da its apparent and Dt its true density, N its apparent and Ns its true refractive index, Vs and Vp the volumes of solid and pore-space respectively in a given volume of porous solid, and Np the refractive index of air.

The results of both calculations appear in table II. There is some correspondence between the determined and calculated refractive indices of the quartz-rich material; this is more marked from 600° to 1000° C., i.e. along the near-horizontal portion of the temperature-density curve. The cristobalite-rich material also shows correspondence which is particularly close for the cristobalite recrystallized at 1000° C. with 2 % of sodium carbonate.

Colour.—An endeavour was made to oxidize the carbonaceous matter in the flint without employing elevated temperatures. This was done by soaking small chips in 100 volume hydrogen peroxide for six months. The supernatant liquid was replaced by fresh hydrogen peroxide about every week. At the end of the treatment the flint had become distinctly paler by incident light. This effect may arise, however, merely by the soaking of liquid into a porous structure; it may be comparable, for instance, with the transparency caused by steeping air-dried hydrophane or tabashir in water (cf. Ostwald, 1924). Such an explanation of the results is, however, unlikely, because prolonged boiling of flint chips in water containing a wetting agent, under a reflux condenser, produced no obvious fading of the colour seen by incident light.

The whitening of flint which accompanies calcination became significant at 400° C. and was especially obvious in the range 500–600° C.

Holdridge et al. noticed that flint shattered markedly at about 365° C., i.e. near the critical temperature of water; our own experience has been similar.

Of some interest is the peculiar patchy brownish colour which calcined flint exhibits by transmitted light even in sections or grains only 30–40 microns thick. The colour was incipient at 400° C., marked at 500° C., and strong at 600° C. and upwards to 1400° C., irrespective of whether the particles were quartz or cristobalite. The observations were made on particles which had passed a 200-mesh B.S. sieve. Thin sections even of raw flint may be found to transmit a very pale straw colour if they are examined microscopically with a low-powered objective.

The colour may depend on the presence of foreign material, probably iron, or, alternatively, it may be caused by peculiarities in the fine structure of the calcined flint itself. That iron may be involved is suggested especially by the results of Hedvall and Sjöman (1931). They found that, if the changes low-quartz → high-quartz or low-cristobalite → high-cristobalite occurred in the presence of ferric oxide, there was definite interaction between the silica and the iron compound. In particular the change quartz → cristobalite led to the formation of a reddish product which was presumably a ferriferous solid solution.

An attempt was therefore made to remove iron from the flint and to decide if such removal weakened the brownish colour of the calcined material. Flint was calcined at 500° C. and then finely powdered; the grains of powder transmitted a strong brownish colour. The powder was heated in streams of chlorine at temperatures up to 550° C. or of carbon tetrachloride vapour (i.e. probably chlorine and phosgene) at temperatures up to 700° C. Such treatment was maintained for six hours; by this time water through which the issuing gases had bubbled gave no further reactions for iron. The flint from several experiments showed no fading of the initial brownish colour (contrast the bleaching of the rutile similarly treated by Williamson, 1940).

The second hypothesis, i.e. that the brown colour depends on the structure of the solid, must be considered the more probable. The brown colour may be equated with the yellowish-red colours which, as Ostwald (1924, p. 391) remarked, are transmitted by many dispersions.

In these laboratories brownish colours, visible in transmitted light, have been produced by a variety of processes:

(*a*) The 'smoking' of glass by the fumes from burning magnesium.

(*b*) The acidification of solutions of sodium thiosulphate (cf. Bancroft and Gurchot, 1932).

(*c*) The dehydration of silica-gel; the colour disappears when the gel is rehydrated.

(*d*) The incipient devitrification of glass by appropriate heat-treatment.

All the examples cited by Ostwald or by ourselves involve a phase which is finely dispersed through or on another phase. The example most directly comparable with calcined flint is dry silica-gel which presumably contains gas-filled pores in a solid medium. A behaviour like that of flint has been noticed in topaz by Bradley, Schroeder, and Keller (1940). On calcination this mineral acquired a tan or light-brown colour which appeared to depend mainly on the presence of submicroscopic pores and cracks caused by the loss of volatiles. Endell and Rieke (1913) had stated that the internal cracking of heated silica produced an optical effect which gave the impression of isotropism when the material was examined with the microscope; they did not mention specifically the brownish colour here described. It has been noticed in the present investigation that this colour interferes appreciably with the recognition of birefringence. Williamson (1941) has already discussed some factors which may cause the appearance of a real or apparent isotropism in calcined flint.

Calcined flint is a solid which contains gas-filled or empty pores. Thus the brownish transmitted colour is not caused by the Christiansen effect (Ostwald, 1924; Raman and Ramaseshan, 1949; Woods, 1934), because this requires, among other prerequisites, two phases of different dispersive power but having a common refractive index in some part of the spectrum.

If the brownish colour can be regarded as an impure yellow-orange, produced because the pores in the flint vary somewhat in dimensions, a comparison with the well-known findings of Rayleigh is invited. Rayleigh's mathematical thesis indicated that the light transmitted through a heterogeneous system of appropriate granularity is richer in the radiation of longer wave-lengths; that scattered is richer in the radiation of shorter wave-lengths. The light scattered by the pores in flint should thus be richer in blue, but this was not demonstrable in the few simple experiments which were made; cracks in the flint appeared to reflect sufficient white light from their walls to conceal any blueness from the eye. Bancroft and Gurchot (1932), however, have cited heterogeneous systems in which a change in the size of the dispersed phase has caused

a systematic alteration in the colours transmitted. This would be expected from Rayleigh's findings, but the colours may arrange themselves in successive series which, furthermore, may show a repetition which is nearly regular. Brown colours (cf. flint, &c.) may be represented in these series. It does not seem possible to deduce such colour series from Rayleigh's equations which, in their present form, apply only to a limited range of sizes. Shoulejkin (1924) has now extended Rayleigh's mathematical treatment to the study of particles of any size (see also Sinclair and La Mer, 1949, for a bibliography of light-scattering phenomena). We, however, do not feel competent to pursue this discussion further.

It was mentioned earlier that the brown colour persisted even in flint calcined at 1400° C., i.e. in cristobalite. If the colour depends on the presence of minute pores, the recrystallization processes, which convert this cristobalite to material of higher density and refractive index, should lead to a disappearance of the colour. This was confirmed. Recrystallization in the presence of 2 % of sodium carbonate (see above) gave a colourless cristobalite although the process, as indicated by the somewhat low density of the material, was incomplete. It could, of course, be argued that a foreign tinctorial agent had left the crystals and had become concentrated in the small amount of soda-rich phase produced. However, similar results followed the recrystallization, at temperatures somewhat greater than 1500° C., of flint with no added fluxes. The recrystallized material was often clear although there were many turbid grains. The turbidity depended on the presence of collections of obvious cavities. The typical brown colour had, however, disappeared.

In conclusion, the possibility may be noted that the brownish colours seen in thin sections of some natural or artificial products may result from an optical phenomenon of the type discussed above, e.g. certain opals, volcanic glasses, and felspars (MacGregor 1931, p. 525) and the fine-textured partially glassy matrix of many whiteware and other ceramic 'bodies'. Further, it may be significant that the collophane described by Dunham, Claringbull, and Bannister (1948) as having a low refractive index, dependent on porosity, is brown in thin section.

Summary.

(1) Cretaceous flint from the sea-beaches of England was shown by X-ray powder photography to consist of quartz of which much was very fine-grained. Opal or cristobalite, if present, were in amounts

too small for detection. The flint had the microscopical characteristics of chalcedony.

(2) Included calcareous matter, of which some was the undoubted remains of fossils, had been partially replaced by silica. This was well displayed by an aggregate of eumorphic carbonate, with Fe, Mg, and Ca, of which part had been converted to pseudomorphs of quartz.

(3) A chemical analysis and a continuous weight-loss versus temperature curve are presented for the flint. The obstinate retention of water at elevated temperatures does not in itself imply the presence of opal; adsorption and occlusion in a fine-grained system could suffice to give this effect.

(4) In the raw state the flint was blackish by incident light. Prolonged treatment with hydrogen peroxide caused a fading of this colour. After adequate calcination the flint was white by incident light, but brown by transmitted light even at thicknesses of 30–40 microns.

(5) Calcination caused also a decrease in density and refractive index. The density-temperature curve declined steeply from 300° to 600° C. and then much more slowly to 1000° C. A further sharp fall succeeded from 1100° to 1400° C. This second fall was caused by the formation of cristobalite; below 1200° C. quartz alone was detected by X-ray powder photography.

(6) The density-temperature and refractive index-temperature curves showed a general similarity of shape.

(7) The cristobalite formed at 1400° C. was of anomalously low density and refractive index.

(8) Anomalously low densities and refractive indices were shown by flint calcined at various temperatures irrespective of whether quartz or cristobalite was present. These properties were attributed to the presence of minute pores.

(9) To the pores was ascribed also the brown colour by transmitted light which accompanied the anomalous properties mentioned and appeared in both quartz-rich and cristobalite-rich preparations. Recrystallization of the cristobalite prepared at 1400° C. increased the density and refractive index and discharged the brown colour; these effects are explicable by the removal of minute pores. Comparable examples of the production of brownish colours in dispersions are enumerated; some are of geological interest.

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prepared and interpreted weight-loss curves and X-ray photographs and helped us also by constructive criticism.

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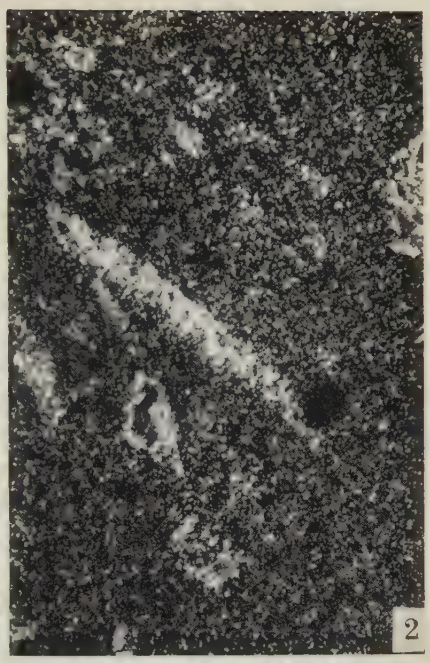

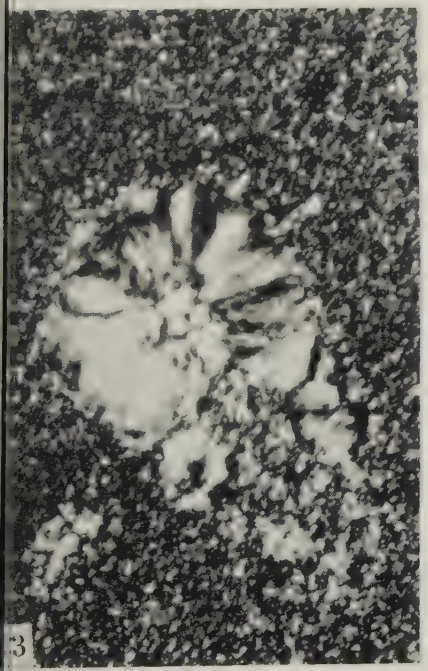

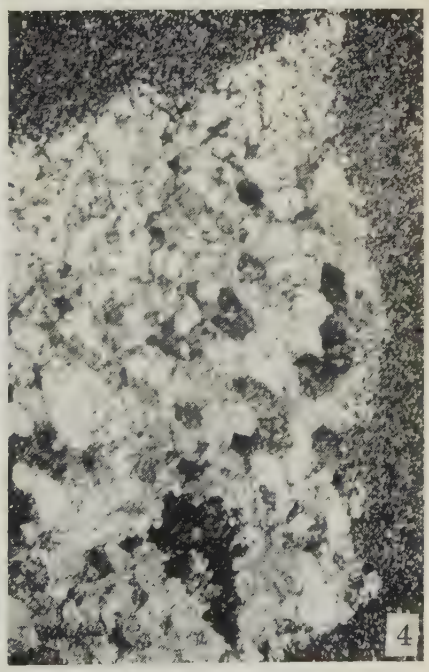

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Explanation of Plate XIV.

Photomicrographs of flint.

Fig. 1. Foraminiferal shell in flint. The central portion i still calcareous, the rest siliceous. ×153.

Fig. 2. Elongated body consisting of fibrous chalcedony. Some of the coarser areas elsewhere contain rhombohedral carbonate. ×80.

Fig. 3. Chalcedony fibres diverging from the boundary between the 'matrix' and coarser aggregate. ×130.

Fig. 4. Inclusion in flint. Eumorphic rhombohedral carbonate partially replaced by quartz near the boundary with the 'matrix'. ×51½.

A new occurrence of uvarovite from northern Karelia in Finland.

(With Plate XV.)

By Oleg von Knorring, M.Sc.

Department of Geology, The University of Leeds.

[Communicated and read by Prof. W. Q. Kennedy, March 8, 1951.]

In 1929 Väyrynen[1] discovered a chalcopyrite-bearing pyrrhotine deposit at the village of Luikonlahti, 30 km. NW. of the Outokumpu mine. This occurrence is associated with a complex of serpentine, quartzites, phyllites, dolomites, and diopside-tremolite-rocks, together with penetrating granites, aplites, and pegmatites. The rock association thus closely resembles that of the Outokumpu ore-field.

In 1947, during a geological excursion to north Karelia, under the direction of Professor Eskola, the writer collected material from Luikonlahti mine containing large amounts of uvarovite. Two main types of uvarovite-bearing rocks are represented:

1. A glassy, dark-grey quartzite, impregnated with excellent tiny crystals of pyrrhotine and irregular aggregates of uvarovite.
2. A pyrrhotine ore with diopside and uvarovite.

Although lacking the brilliant emerald-green colour of the Outokumpu uvarovite-rocks these types are nevertheless more impressive in that the uvarovite occurs as a true 'rock-forming' mineral.

The main interest naturally attaches to the composition and properties of the uvarovite, and it is with these mineralogical and chemical aspects that the following investigation is mainly concerned. For comparative purposes a uvarovite garnet from Outokumpu has also been investigated.

Petrographical characters of the uvarovite-bearing rocks.

The three main rock types employed in the investigation were:

1. Quartzite, with pyrrhotine and uvarovite, from Luikonlahti.
2. Pyrrhotine ore, with uvarovite and diopside, from the same locality.
3. Quartzite, with uvarovite, diopside, tremolite, calcite, and some pyrrhotine, from Outokumpu.

[1] H. Väyrynen, On the geology and tectonics of the Outokumpu ore field and region. Bull. Comm. Géol. Finlande, 1939, no. 124.

1. In hand-specimen the quartzite from Luikonlahti is a glassy, dark grey unstratified rock impregnated with tiny (1–2 mm.) crystals of pyrrhotine and small aggregates of uvarovite up to 10 mm. in diameter. Under the microscope, quartz as irregular grains, usually with undulating extinction, is seen to be the main constituent. Uvarovite occurs in aggregates following the boundaries between the quartz grains (pl. XV, fig. 1) and is almost invariably slightly anisotropic. Pyrrhotine forms perfect six-sided crystals, many of which contain a tiny central inclusion of quartz. In addition to these main constituents very subordinate amounts of diopside, radiating fibrous tremolite, and calcite are also present.

2. The uvarovite-bearing pyrrhotine ore from Luikonlahti is somewhat variable in constitution, but usually contains approximately equal amounts of pyrrhotine, uvarovite, and diopside; in certain specimens, however, the silicates may predominate. The uvarovite forms patches up to 1 cm. in diameter.

Under the microscope two generations of uvarovite can be distinguished. The garnet of the first generation is normally partly decomposed and may be represented only by very fine-grained aggregates of diopside and tremolite containing fringed relict grains of uvarovite. The shapes of the original crystals can, however, be clearly recognized under crossed nicols. Uvarovites of the second generation are fresh and contain no inclusions. They occur sometimes as perfect crystals, with only the edges altered (pl. XV, fig. 2) and often surround partly decomposed uvarovites of the first generation. Both isotropic and anisotropic types of uvarovite have been observed and in a few cases excellent zoning occurs (pl. XV, fig. 4). Very often the central part of the garnet crystal only is anisotropic and zoned.

The diopside forms well-developed crystals and is almost always twinned. Sphene is quite abundant, usually in cracks, and tremolite has also been identified. Chalcopyrite is a fairly common constituent in some specimens, and, more rarely, molybdenite has also been found.

3. The specimen from Outokumpu, taken for comparison, is a glassy quartzite with fine-grained diopside-tremolite bands containing scattered grains of uvarovite and chromite. Excellent crystals (110) and (112) of uvarovite with striated faces, up to 1·5 cm. in diameter, occur in pockets of coarse-grained calcite, and are associated with irregular patches of pyrrhotine, which may show small inclusions of uvarovite.

Under the microscope it is apparent that the uvarovite normally occurs in a groundmass of quartz, diopside, tremolite, and calcite. In

this case also two generations of uvarovite can be distinguished. The earlier generation, which appears to have developed from chromite, is often isotropic and contains cracks, and inclusions of calcite (pl. XV, fig. 5). The second generation forms more massive crystals, is usually anisotropic, and is devoid of chromite relicts. The original crystal boundaries of the first-generation uvarovite can be clearly recognized under crossed nicols, and these ghost-like uvarovites are invariably seen to be surrounded by fresh uvarovite of the second generation (pl. XV, fig. 6).

Grains of chromite in various stages of alteration are abundant in the uvarovite, and chromite is also found independently as well-preserved crystals. In certain cases, cracks in the chromite are filled with uvarovite, diopside, tremolite, and calcite (pl. XV, fig. 5). Finally, chromite occurs as inclusions in uvarovite either in the form of rounded and perforated crystals and irregular grains or as a dust-like product.

Chemical investigation.

Chemical analyses were carried out on carefully separated and hand-picked material from the three specimens, and the results are given in table I. In each case 0·5 gram of substance was used. Chromium was determined volumetrically, and aluminium in the usual manner by difference from the sesquioxides.

Menzer[1] has shown that the cubic unit cell of garnet contains eight molecules of composition $R_3^{2+}R_2^{3+}[SiO_4]_3$. Accepting, as a basis for calculation, the presence of 96 oxygen atoms in a unit cell, it is possible to calculate (from the chemical analyses) the corresponding numbers of atoms of the other elements present. These results are given in table II.

These analyses represent isomorphous mixtures of uvarovite and grossular with some andradite. In the garnets from Luikonlahti the proportion of uvarovite to grossular is about 1 : 1 as against a proportion of 3 : 1 in the new analysis of uvarovite from Outokumpu.

The Cr_2O_3 content of the analysed uvarovites ranges from 12·25 to 22·60 %, and the corresponding Al_2O_3 content from 12·00 to 5·34 %. The iron content is fairly low in all cases. Compared with previous analyses of uvarovite from Outokumpu, viz. analyses 4 and 5, the main difference lies in the chromium and aluminium contents.

[1] G. Menzer, Die Kristallstruktur der Granate. Zeits. Krist., 1928, vol. 69, pp. 300–396. [M.A. 4–111.]

TABLE I. Chemical analyses of uvarovite.

	1.	2.	3.	4.	5.
SiO_2	38·68	38·40	37·31	35·88	36·79
Al_2O_3	12·00	10·77	5·34	1·13	1·93
Cr_2O_3	12·25	14·97	22·60	27·04	27·54
Fe_2O_3	2·47	1·89	0·30	2·46	0·41
MnO	n.d.	n.d.	0·15	0·03	—
MgO	0·20	0·48	0·25	0·04	0·50
CaO	34·04	33·08	34·25	33·31	32·74
Mn.	0·20	0·40	0·10	0·18	—
	99·84	99·99	100·30	100·07	99·91

1. Uvarovite in pyrrhotine-quartzite, Luikonlahti, Finland. Analyst: O. von Knorring.
2. Uvarovite in pyrrhotine-diopside ore, Luikonlahti, Finland. Analyst: O. von Knorring.
3. Uvarovite in diopside-tremolite skarn, Outokumpu, Finland. Analyst: O. von Knorring.
4. Uvarovite in uvarovite-tremolite-tawmawite-pyrrhotine vein, Outokumpu, Finland. Analyst: L. Lokka (in P. Eskola, 1933)[1].
5. Uvarovite in quartzite, Outokumpu, Finland. Analyst: L. H. Borgström.[2]

TABLE II. Number of atoms (O = 96) in unit cell of uvarovite.

	1	2	3	Theoretical
O	96	96	96	96
Si	24·33	24·28	24·14	24
Al	8·88	8·00	4·08	—
Cr^{3+}	6·08	7·46	11·56	—
Fe^{3+}	1·16	0·90	0·14	—
	16·12	16·36	15·78	16
Mn	—	—	0·18	—
Mg	0·18	0·45	0·24	—
Ca	22·93	22·40	23·73	—
	23·11	22·85	24·15	24

The diopside from sample no. 2 was analysed, mainly as a check for chromium, and the Cr_2O_3 content was found to be very small indeed, less than 0·01 %. The composition of this diopside is shown in table III: together with an analysis of chrome-diopside from Outokumpu for comparison.

[1] P. Eskola, On the chrome minerals of Outokumpu. Compt. Rend. Soc. Géol. Finlande, 1933, no. 7, pp. 26–44. [M.A. 6–46.]

[2] L. H. Borgström, Uwarowit från Kuusjärvi. Geol. För. Förh. Stockholm, 1901, vol. 23, pp. 560–563.

TABLE III. Chemical analyses of diopside.

		1.	2.
SiO_2	...	53·20 %	52·84 %
Al_2O_3	...	0·76	1·04
Cr_2O_3	...	0·00*x*	0·44
FeO	...	6·06	2·52
MgO	...	15·59	17·26
CaO	...	24·70	25·44
H_2O	...	—	0·88
		100·31	100·42

1. Diopside in uvarovite-pyrrhotine ore, Luikonlahti, Finland. Analyst: O. von Knorring.

2. Diopside in diopside skarn, Outokumpu, Finland. Analyst: E. S. Tomula (in P. Escola, 1933, loc. cit.).

Determination of the refractive index and specific gravity of the analysed uvarovite garnets.

Ford,[1] Fleischer[2] and others have shown that the optical and physical properties of a garnet are directly dependent on its chemical composition. In the case of uvarovite, however, exceptionally few cases are known in which the chemical composition, refractive index, and specific gravity have been determined on the same specimen. It is desirable, therefore, to obtain all possible physical data for the three analysed uvarovite garnets. According to Ford the calculated refractive index for an ideal uvarovite is 1·870, a value which is based on only one determination.

Anomalous birefringence introduces certain difficulties in refractive index determination on uvarovite and, in addition, the analysed material was too brittle to make prisms. The indices were, therefore, determined by the immersion method in sodium-light using phenyldiiodoarsine with methylene iodide. The results of these determinations are listed in table IV. When the maximum values obtained are plotted against the corresponding Cr_2O_3 content (fig. 1) an almost perfect linear relationship is seen to exist between the refractive index and chemical composition of uvarovite, despite small differences in the iron content. It is apparent from these results that the value 1·870 for uvárovite, as quoted in text-books, is too high. The specific gravity of the analysed uvarovites were

[1] W. E. Ford, A study of the relations existing between the chemical, optical and other physical properties of the members of the garnet group. Amer. Journ. Sci., 1915, ser. 4, vol. 40, pp. 33–49. [M.A. **2**–37.]

[2] M. Fleischer, The relation between chemical composition and physical properties in the garnet group. Amer. Min., 1937, vol. 22, pp. 751–759. [M.A. **7**–109.]

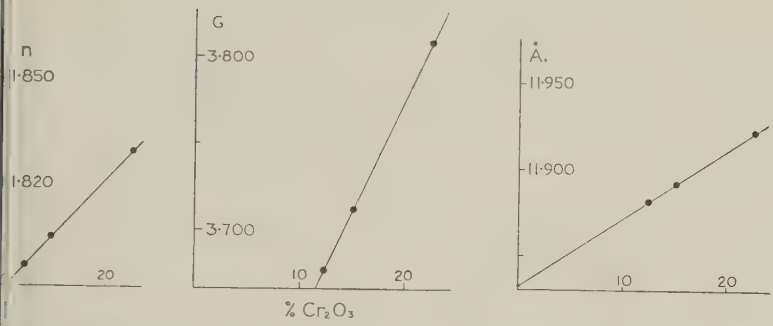


FIG. 1. Variation of the refractive index, specific gravity, and edge of unit-cell dimensions with chromium content.

Determined by means of a pyknometer, using toluene as displacement liquid. The results are compiled in table IV, again showing a linear relationship.

TABLE IV. X-ray, optical, and specific gravity data for uvarovite.

	Mol. wt.	*a*.	Sp. gr.	*n*.
Luikonlahti no. 1	470·2	11·881 Å	3·676	1·796
Luikonlahti no. 2	472·4	11·892	3·712	1·798–1·804
Outokumpu no. 3	487·6	11·922	3·809	1·821–1·829
Outokumpu (Menzer)	495·2	11·950	3·805	1·8516

X-ray study of the analysed uvarovites.

According to Stockwell[1] the first X-ray study on garnet (an almandite-spessartine) was made by Nishikawa in 1917 and, later, Menzer (loc. cit.) carried out a complete investigation of the six main garnet species. Subsequently Stockwell pointed out that a linear relationship exists between the edge length (*a*) of the unit cell and the chemical composition within the garnet group. In the case of the material under investigation two garnet molecules are involved, viz. uvarovite and grossular. In order to obtain a complete picture of the comparative relationship between these garnet molecules, the edge lengths of the analysed uvarovites and of a pink grossular from New Mexico were determined.

In fig. 1 the dimensions of *a* so obtained are plotted against the Cr_2O_3 content of the uvarovites. The four points of the corresponding garnets all lie almost exactly on a line. Menzer (loc. cit.) obtained somewhat higher values of *a* both for grossular and uvarovite, but in spite of

[1] C. H. Stockwell, An X-ray study of the garnet group. Amer. Min., 1927, vol. 12, pp. 327–344. [M.A. 3–433.]

this, a line through the values obtained by Menzer, is almost parallel to the former. There can, therefore, be little doubt concerning the existence of a linear relationship between the edge length of the unit cell and the chemical composition of the garnets, as Stockwell has pointed out.

General considerations.

The most significant features of the geology and genesis of uvarovites from Luikonlahti and Outokumpu are their association with serpentine intrusions. Thus the source for the element chromium seems to be determined. However, very little is known concerning the active mode of introduction of chromium into the various uvarovite-bearing rocks. The present investigation provides some evidence on this problem.

Uvarovite has undoubtedly been formed in different ways and during various stages of metamorphism. In specimen no. 2, from Luikonlahti (containing uvarovite, diopside, and pyrrhotine) the first-generation uvarovite was apparently formed at the same time as the associated skarn minerals, and probably as one of the first as it appears to precede diopside, tremolite, and the other silicates. It must be assumed in this case that the chromium was introduced from the associated ultrabasic rocks. The second-generation uvarovite developed during the deposition of pyrrhotine, the chromium metasomatism being connected with the ore genesis. The uvarovite from the Luikonlahti quartzite is also associated with pyrrhotine and must be similar in genesis to this later type.

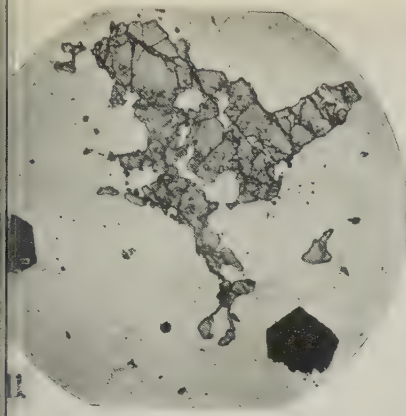
In the material from Outokumpu the first generation of uvarovite is undoubtedly a replacement product of the chromite, whereas the second generation is again intimately connected with the formation of ore minerals.

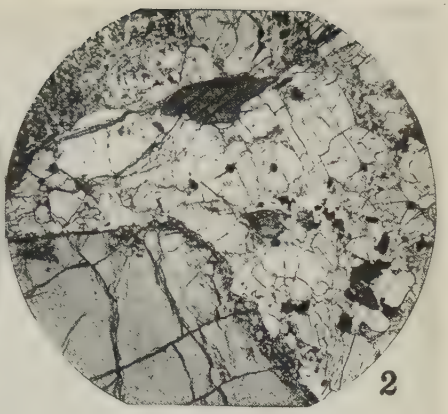
Eskola (loc. cit.) states that the skarn-mineral association is connected with the dolomites in Outokumpu. He also describes a peculiar occurrence of dolomite containing chromite, which association has, however, been found only in one place, whereas chromite-free dolomites have been observed quite frequently.

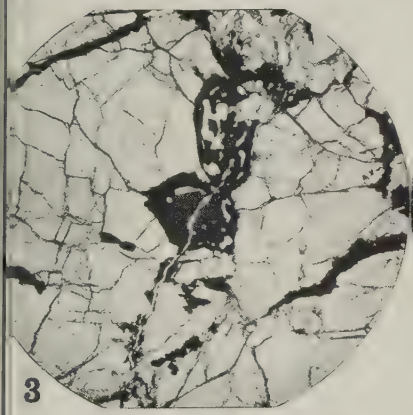
On the assumption that dolomites containing chromite have reacted during a stage of metamorphism with silica in the presence of water, the following reaction could occur:

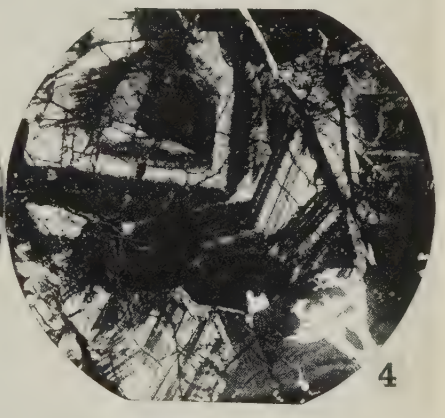
Dolomite + chromite + SiO_2 + H_2O → tremolite + diopside + uvarovite.

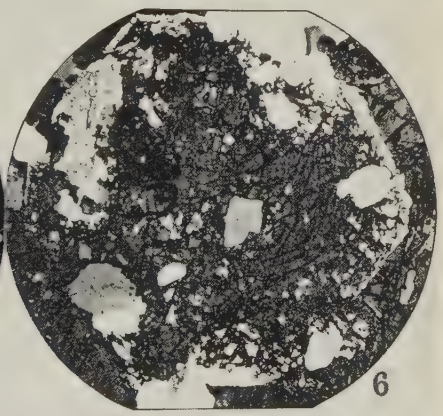
Eskola mentions that the chromite is unevenly distributed in the dolomite, an observation which is in good agreement with the uneven distribution of chromium in the skarn.











O. von Knorring: Uvarovite from Karelia

The aluminium content in uvarovite, tremolite, and diopside is partly derived from aluminium-bearing chromite and partly from aluminium present in the rock itself. If the chromite in dolomite is of a hydrothermal origin, formed before or during the process of serpentinization, the skarn-mineral association, including uvarovite and also the ore with the second-generation uvarovite, must have formed *after* the serpentinization. A similar origin for uvarovite could be applied to the Luikonlahti locality.

The chemical investigation has shown that the composition of uvarovites from the same locality may vary to some extent. The refractive indices, specific gravities, and unit-cell dimensions, determined on the analysed chrome garnets are directly dependent on the chemical composition.

Acknowledgements.—Thanks are due to Messrs. T. F. Johnston and Mr. W. L. Wilson of this department for their technical assistance during the course of the investigation. The writer is indebted to Mrs. Toini Mikkola of the Geological Survey of Finland in Helsinki for determination of the refractive indices of the analysed uvarovites. A special expression of gratitude is due to Professor W. Q. Kennedy for all the aid and encouragement he has given me throughout the work.

Explanation of Plate XV.

Photomicrographs of uvarovite from northern Karelia, Finland.

Fig. 1. Uvarovite in glassy quartzite from Luikonlahti; the opaque mineral is pyrrhotine. ×19.

Fig. 2. Uvarovite-diopside skarn from Luikonlahti. Euhedral uvarovite in a groundmass of diopside, tremolite, and sphene. The opaque minerals are pyrrhotine, chalcopyrite, and molybdenite. ×19.

Fig. 3. A large uvarovite crystal with typical cracks and patches of pyrrhotine. ×19.

Fig. 4. As in fig. 3. Crossed nicols. ×19.

Fig. 5. Large chromite crystal, with cracks infilled by uvarovite, diopside, and tremolite, in tremolite base. ×19.

Fig. 6. Euhedral uvarovite crystal of the first generation with included chromite relicts, surrounded by second-generation uvarovite. Crossed nicols. ×19.

The use of the gnomonic projection in the determination of the optical indicatrix of crystals.

By N. Joel, M.Sc.

Birkbeck College Research Laboratory, London.

[Taken as read November 2, 1950.]

Introduction.

In a previous paper[1] a description of a method was given which had been developed to determine the indicatrix of small crystals, both in orientation and magnitude, making use of the simple one-circle stage goniometer described by Bernal and Carlisle.[2]

As was explained there, when a crystal is viewed in parallel polarized light, between crossed nicols, the two observed extinction directions are the axes of the ellipse determined by the intersection of the indicatrix with a plane through its centre parallel to the plane of the microscope stage. For each position θ of the goniometer there are two extinction directions (ϕ_1 and ϕ_2) given by the readings on the microscope. These directions can be represented on a stereographic projection at suitable intervals of θ. It was shown there that the curves determined (on the indicatrix and on the stereographic projection) by these extinction directions during a complete rotation of the indicatrix about its fixed but arbitrary axis must contain the points representing the axes X, Y, and Z of the indicatrix. Furthermore, it was shown how to determine the actual orientation of these three axes and to measure the corresponding three principal refractive indices.

An attempt is made in the present paper to give the mathematical relations involved in the problem.

Theoretical treatment.

For the sake of simplicity, instead of rotating the indicatrix and studying its central sections parallel to the plane of the microscope stage, let us keep the indicatrix fixed and imagine a plane rotating about

[1] N. Joel, Min. Mag., 1950, vol. 29, p. 206.

[2] J. D. Bernal and C. H. Carlisle, Journ. Sci. Instruments, 1947, vol. 24, p. 107.

n axis which is parallel to the axis of the stage goniometer and goes hrough the centre of indicatrix. Moreover, let us imagine the indicatrix xed with its Z-axis vertical. The rotation axis of the stage goniometer ill no longer be horizontal, but will have an arbitrary—but fixed-- rientation.

The equation of the indicatrix, with refractive indices equal to α, β, nd γ along the X, Y, and Z axes, in cartesian co-ordinates, is

$$Ax^2+By^2+Cz^2 = 1, \tag{1}$$

here for simplicity (and throughout the whole paper), A, B, and C and for α^{-2}, β^{-2}, and γ^{-2}, respectively.

Consider on the indicatrix the curves of constant refractive index. hey are the intersections of surface (1) and the surfaces

$$x^2+y^2+z^2 = n^2, \tag{2}$$

here n is the refractive index and takes any value between α and γ. hey are better represented in polar co-ordinates. If μ is the polar ngle, measured from the Z-axis, and λ the azimuthal angle, measured rom the X-axis towards the Y-axis, the equation is

$$\sin^2\mu = \frac{N-C}{A-C-(A-B)\sin^2\lambda}, \tag{3}$$

where N stands for n^{-2}. The rotation axis of the goniometer will be epresented by its polar co-ordinates λ_0 and μ_0.

For the mathematical study of this particular problem the gnomonic projection is much more convenient than the stereographic projection, s the constant refractive index curves become conic sections and the otating plane becomes a straight line rotating about a point.

If, for instance, the plane of the gnomonic projection is chosen perpendicular to the Z-axis of the indicatrix, at an arbitrary distance d rom the XY plane, and its X and Y axes are chosen parallel to the X nd Y axes of the indicatrix, the equation of the constant refractive ndex curves is:

$$(A-N)x^2+(B-N)y^2+(C-N)d^2 = 0. \tag{4}$$

The curves are ellipses for $C < N < B$ (that is $\beta < n < \gamma$); hyperbolae or $B < N < A$ ($\alpha < n < \beta$); and a pair of parallel straight lines,

$$x = \pm\frac{B-C}{A-B}d,$$

for $N = B$ ($n = \beta$), which are the projections of the two circular sections of the indicatrix (fig. 1).[1]

Consider, in fig. 1, any straight line. It represents a given section of the indicatrix and is a tangent to two of the constant refractive index curves (as will be shown below). The two contact points obviously represent the points of maximum and minimum refractive index along

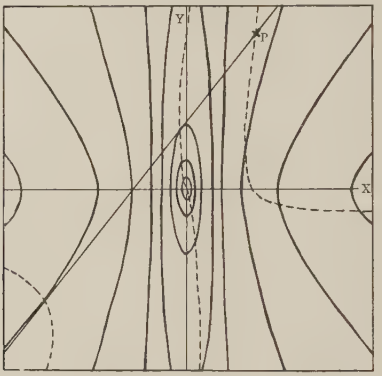


FIG. 1.

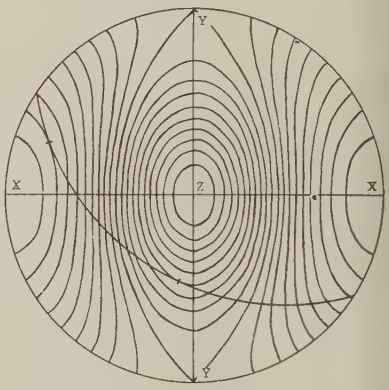


FIG. 2.

FIG. 1. The constant refractive index curves in the gnomonic projection for arbitrarily chosen values of α, β, and γ. The refractive index decreases from γ to α along the X-axis, and from γ to β along the Y-axis. Point P represents the goniometer axis, and the line through P, a section of the crystal. The dotted curves are the vibration-direction curves (or extinction-direction curves) for the given position of P.

FIG. 2. Stereographic projection of the curves of constant refractive index for a crystal with $A-B = B-C$, that is $2V = 90°$. The curves are drawn at regular intervals of N. Sections of the crystal are represented by great circles.

that line and therefore represent the two vibration directions in that given section. (It is easy to show that they are always 90° apart.) It follows that if a line rotates about a fixed point in the gnomonic projection (which corresponds to a plane rotating about the stage goniometer axis), the locus of the contact points will be the extinction-direction curve (or vibration-direction curve) mentioned in the first paper. Naturally the same holds for the stereographic projection, where it is a great circle that rotates about a fixed point.

[1] It should be noted that whatever the direction chosen for the plane of the gnomonic projection, the constant refractive index curves will always be conic sections. Their equations may be completely different, but the problem remains essentially the same.

We shall represent the rotation axis by the point $P(x_0, y_0)$, where $x_0 = d \tan \mu_0 \cos \lambda_0$; $y_0 = d \tan \mu_0 \sin \lambda_0$.

The tangents drawn from the point P to one of the curves (4) have contact points (x_1, y_1) and (x_2, y_2) given by

$$\left.\begin{aligned}(A-N)x^2+(B-N)y^2+(C-N)d^2 &= 0\\ (A-N)x_0 x+(B-N)y_0 y+(C-N)d^2 &= 0\end{aligned}\right\}. \tag{5}$$

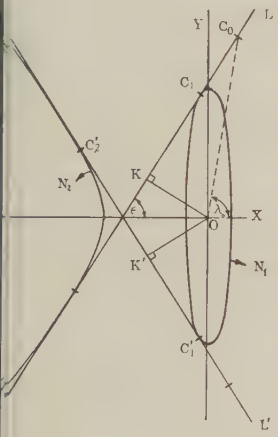


FIG. 3.

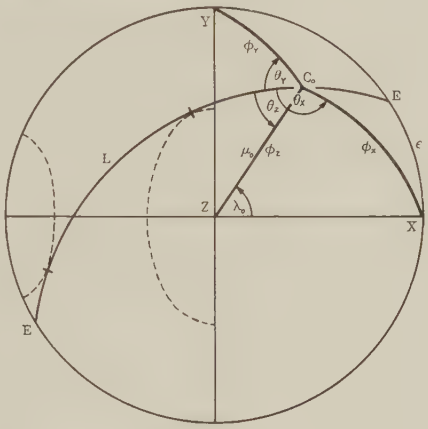


FIG. 4.

FIG. 3. Graphical construction (in gnomonic projection) to determine the orientation of the goniometer axis (C_0) with respect to the indicatrix.

FIG. 4. Diagram illustrating the change of the plane of the stereographic projection from the position normal to the Z-axis of the indicatrix to a plane parallel to the microscope stage. The polar angles ϕ are measured from the goniometer axis (C_0), and the azimuthal angles θ are measured from the plane of the microscope stage (great circle L).

When the line rotates about P, the locus of those contact points is obtained by eliminating N from the two equations (5)

$$(A-B)x_0 xy^2-(A-B)y_0 x^2 y-(B-C)d^2y^2-(A-C)d^2x^2 +(B-C)d^2y_0 y+(A-C)d^2x_0 x = 0, \tag{6}$$

or

$$(A-B)(x_0 y-y_0 x)xy+d^2(B-C)(y_0-y)y+d^2(A-C)(x_0-x)x = 0.$$

In fig. 1 the curve (6) corresponding to the given position of P is shown.

A line $y-y_0 = m(x-x_0)$ is a tangent to two of the constant refractive

index curves (one ellipse and one hyperbola); their two N-values are the solutions of

$$pN^2-qN+r=0, \tag{7}$$

where

$$p = d^2+m^2d^2+(y_0-mx_0)^2,$$

$$q = d^2(A+C)+m^2d^2(B+C)+(y_0-mx_0)^2(A+B),$$

$$r = d^2AC+m^2d^2BC+(y_0-mx_0)^2AB,$$

and they correspond to the two refractive indices of that particular section of the indicatrix.

Conversely, if A, B, C, N_1, and N_2 are given, it is possible to determine the equations of the common tangents to the two curves, and the co-ordinates of the contact points.

Practical application.

The above considerations, apart from explaining the behaviour of the indicatrix in the procedure of the method given in the previous paper, suggest, amongst other possibilities, the following application.

In order to find the optical orientation of a crystal of known optical constants, the answer may be obtained by following the method described in the previous paper, with small variations.

But, if for any reason (the crystal's shape, for instance) the crystal cannot be turned freely in the liquid, the following method is suggested:

(*a*) Mount the crystal on the goniometer.

(*b*) Fix the stage goniometer in a convenient position θ_0.

(*c*) Note the reading ϕ_0 on the microscope when the light transmitted by the polarizer vibrates parallel to the axis of the stage goniometer, and the ϕ_1 and ϕ_2 readings for the crystal in extinction position.

(*d*) Measure the two refractive indices of that given section and note whether they increase or decrease when the stage goniometer is turned slightly in an arbitrary sense.

(*e*) Choosing a convenient scale, draw the constant refractive index curves $(A-N)x^2+(B-N)y^2+(C-N)d^2=0$ for the two measured refractive indices,[1] and, to those two curves, draw the pair of common

[1] If many sections of the same crystal have to be studied, it is worth while to start drawing a complete chart for the given values A, B, and C at suitable intervals of N, either in the stereographic or in the gnomonic projection. If many sections of different crystals have to be examined, one single chart (in gnomonic projection) drawn for any arbitrary values of A, B, and C (for instance $A-B=B-C$, that is $2V=90°$) may be used by altering the scale of the co-ordinates and choosing the

ngents that are not parallel to each other (fig. 3). Alternatively, stead of drawing the two conics, given A, B, C, N_1, and N_2, the co-rdinates of the four contact points may be calculated.

(f) From the measured refractive indices and the values of ϕ_0, ϕ_1 and $_2$, ϕ_1 may be associated to the contact points C_1 and C_1', ϕ_2 to C_2 and C_2', nd it is possible to decide in which one of the three regions of each ngent line lie the points C_0 and C_0' (the eventual rotation axes) asso-ated to ϕ_0.

(g) If a gnomonic net is available, the actual position of C_0 and C_0' ll be easy to find. In the absence of a net, draw to the line C_1C_2 the rpendicular OK from the origin, and

$$\overline{KC_0} = \sqrt{(d^2+\overline{OK}^2)}.\tan[\alpha+(\phi_0-\phi_1)],$$

here $$\alpha = \tan^{-1}[\overline{KC_1}/\sqrt{(d^2+\overline{OK}^2)}],$$

nd, of course, $$\overline{K'C_0'} = \overline{KC_0}.$$

(h) To decide which of the two tangent lines actually represents the bserved section of the crystal (which is parallel to the plane of the icroscope stage), rotate the two tangent lines about C_0 and C_0' re-pectively, in the opposite sense to the rotation of the goniometer in (g). The one which gives the same variations as in (d) represents the ction of the crystal and also the plane of the microscope stage. Let s suppose it is L; then C_0 (x_0, y_0) will be the goniometer axis.

The orientations of the microscope stage and the goniometer axis with spect to the indicatrix have been found. The polar co-ordinates of the xis are: $\tan\lambda_0 = y_0/x_0$; $\tan\mu_0 = \sqrt{(x_0^2+y_0^2)}/d$.

(i) The plane of projection, which for simplicity had been chosen per-ndicular to the Z-axis of the indicatrix, can now be changed to a lane parallel to the microscope stage and the indicatrix referred to it. he three axes of the indicatrix will then have co-ordinates ϕ and θ, here ϕ is the polar angle measured from the goniometer axis and θ ne azimuthal angle measured from the plane of the microscope stage. a gnomonic net is available, either the rotation may be performed

roper N-values. The N-values and the factors (p and q) by which the scales have be altered can be easily found from equations of the type:

$$\frac{p^2(A-N_1)}{A'-N_1'} = \frac{q^2(B-N_1)}{B'-N_1'} = \frac{C-N_1}{C'-N_1'},$$

nd two similar equations with N_2 and N_2'. But if only a small number of sec-ons are examined it is still more practical to draw only the pair of curves for ch case.

by translating the line L to infinity, or the six angular co-ordinates determined with the help of the net.

If no gnomonic net is available it is also possible to make the change by inserting λ_0, μ_0, and ϵ (the angle between L and the X-axis) in a stereographic projection and, either performing the rotation by bringing the great circle L in coincidence with the primitive with the help of a stereographic net, or by directly reading the six co-ordinates on the net (fig. 4).

Alternatively, it is possible to calculate the ϕ and θ of the three axes. They are:

$$\phi_x = \cos^{-1}[\sin\mu_0.\cos\lambda_0], \quad \theta_x = \theta_z + \cot^{-1}[-\cos\mu_0.\cot\lambda_0],$$
$$\phi_y = \cos^{-1}[\sin\mu_0.\sin\lambda_0], \quad \theta_y = \theta_z + \cot^{-1}[\cos\mu_0.\tan\lambda_0],$$
$$\phi_z = \mu_0. \qquad\qquad \theta_z = \cot^{-1}[\cos\mu_0.\cot(\lambda_0 - \epsilon)].$$

The problem can also be solved using only stereographic projections. The two curves to be plotted belong to the family of curves (equation 3), and with a stereographic net it is possible to find the great circle which touches both (fig. 4). The position of C_0 is then easy to find, and the change of primitive is performed as explained.

Acknowledgements.—I am very much indebted to Professor J. D. Bernal for guidance during the course of this work, and particularly for suggesting the use of the gnomonic projection. I also wish to thank Dr. G. Parry for help and advice on the presentation of the paper.

New occurrences of duftite.

(With Plate XVI.)

By G. F. Claringbull, B.Sc., Ph.D., F.G.S.

Department of Mineralogy, British Museum.

[Read November 2, 1950.]

During an examination of the mineral bayldonite,

$(Pb,Cu)_7(AsO_4)_4(OH)_2.H_2O$,

for the purpose of obtaining standard X-ray powder data to compare with supposed single crystals of this species, it was found that a specimen purchased in 1948 as bayldonite from Ojuela mine, Mapimi, Durango, Mexico (B.M. 1948,267) gave a powder pattern related to those of members of the descloizite group and fairly close to but not identical with conichalcite, $CuCaAsO_4OH$. It chanced that about the same time a specimen of a green botryoidal mineral from Brandy Gill, Caldbeck Fells, Cumberland, sent in by Mr. W. F. Davidson for determination was photographed and showed similar variations from the conichalcite pattern. Qualitative spectrographic comparison of the Mapimi and Brandy Gill materials with several conichalcites suggested that the differences in the powder photographs might be due to the presence of lead in the former.

A powder photograph of duftite[1] from the type locality, Tsumeb, South-West Africa (B.M. 1939,225), was then obtained and found to agree closely with that of the Mapimi mineral, while that of Brandy Gill showed some characters of both duftite and conichalcite. All the earlier patterns showed traces of contamination with associated lead minerals, and only after very careful hand-picking under the high-power binocular microscope could samples be obtained which gave really satisfactory agreement. Very careful sampling of further specimens from Cumberland yielded pictures of slightly varying pattern, some of which are closer to the type Tsumeb pattern than the first examined.

It was felt necessary to prove the diagnostic value of the small differences in the powder patterns of duftite and conichalcite by establishing chemically the presence of reasonable quantities of lead in the new duftite specimens, but as the mineral from Mapimi is intimately

[1] O. Pufahl, Centralbl. Min., 1920, p. 295. [M.A. 1–150.]

associated with other lead minerals, and from Brandy Gill as thin coatings also associated with lead minerals, great care was called for in sampling, and only very small quantities of satisfactorily pure material were obtained. Using samples ranging from 0·8 to 4·7 mg. Dr. M. H. Hey kindly made microchemical determinations by the dithizone method[1] with the following results:

	PbO.
Duftite, Tsumeb (B.M. 1939,225)	51 %
,, Mapimi (B.M. 1948,267)	42
,, Brandy Gill (B.M. 1950,444)	39
Conichalcite, Carissa mine, Mammoth, Utah (B.M. 81763) ...	0
Theoretical for duftite ($CuPbAsO_4OH$)	52·3

It is estimated that the accuracy of the determinations is ± 5 %.

Descriptions of the specimens.

Ojuela mine, Mapimi, Durango, Mexico (B.M. 1948,267).—A friable aggregate of colourless to pale brown wulfenite crystals up to 8 mm. in maximum dimension loosely cemented by mimetite as white fibrous aggregations and duftite as bright yellowish-green minute crystals and crystal complexes. The largest duftite crystals are small prisms about 0·2 mm. long and many are as short as 0·07 mm. The length to width ratio is usually between 10 to 1 and 4 to 1. All refractive indices are above 1·848, that of the highest available immersion liquid.

Brandy Gill, Caldbeck Fells, Cumberland (B.M. 1950,440–444, and other specimens belonging to Mr. W. F. Davidson).—Thin botryoidal coatings of duftite varying in colour from pale emerald-green to deep moss-green in association with mimetite, pyromorphite, stolzite,[2] cerussite, malachite, ankerite, and linarite on a quartzose matrix containing galena and chalcopyrite. The small spherulites of duftite are commonly about 0·1 mm. in diameter and show under crossed nicols typical spherulitic crosses. Variations in refractive index within single spherules suggest that the interior is usually more lead rich than the outer shells. Frequently there is a sharp change in refractive index between core and outer coatings, although all may be above 1·848. Outer layers are sometimes below 1·848. Very occasionally minute, approximately single crystals have been observed.

[1] E. B. Sandell, Colorimetric determinations of traces of metals. New York, 1944, p. 286.

[2] Stolzite is new to this locality and good specimens were also exhibited at the meeting on November 2, 1950, by A. W. G. Kingsbury and J. Hartley.

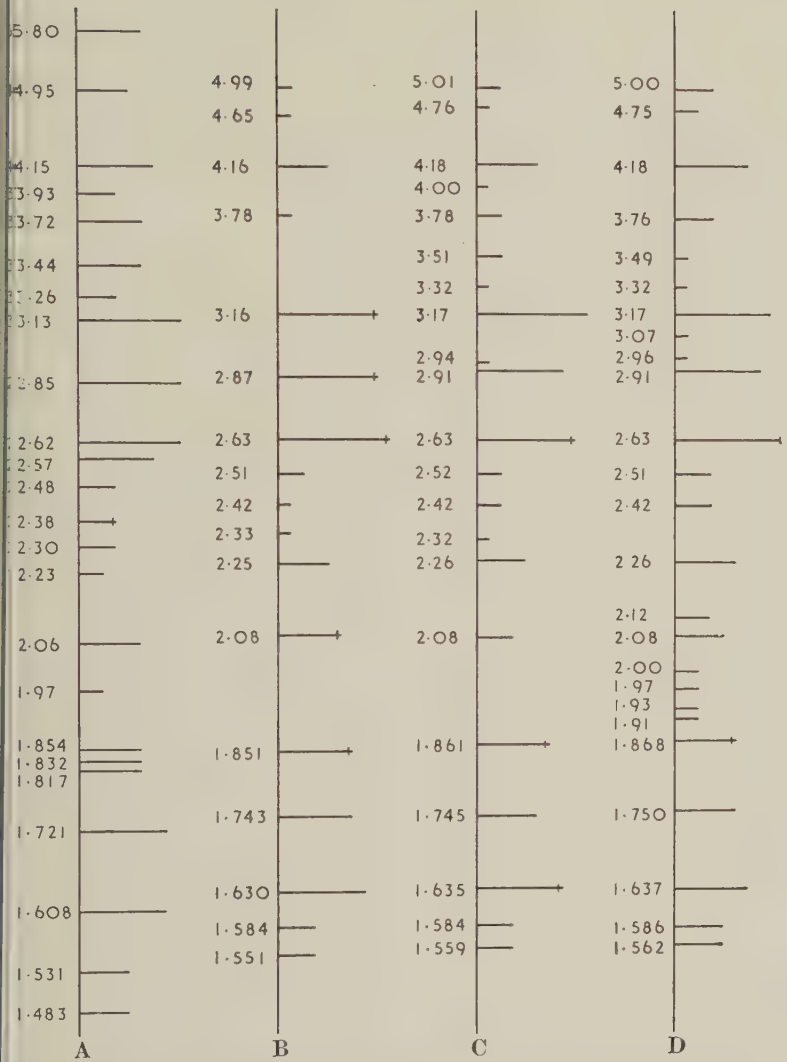


FIG. 1. Spacing-intensity plots of X-ray powder photographs of: (A) conichalcite Bisbee, Arizona (B.M. 1924,696). (B) duftite, Brandy Gill (W. F. Davidson). (C) duftite, Mapimi (B.M. 1948,267). (D) duftite, Tsumeb (B.M. 1939,225).

The *d*-spacings are plotted as reciprocals and their approximate values in Ångström units are given against each line, the length of which is an indication of intensity. A cross-bar indicates a broad and possibly composite line on the photograph. Data derived from table I.

TABLE I. X-ray powder data for conichalcite and duftite in Å.

		Duftite.							Conichalcite, Higgins mine.			
			Tsumeb.		Mapimi.		Brandy Gill.					
hkl.		$d_{calc.}$	*I.*	$d_{obs.}$	*I.*	$d_{obs.}$	*I.*	$d_{obs.}$	$d_{calc.}$		*I.*	$d_{obs.}$
001		—	—	—	—	—	—	—	5·81		m	5·80
011		4·95	w	5·00	vw	5·01	vvw	4·99	4·94		mw	4·95
101		4·64	vw	4·75	vvw	4·76	vvw	4·65	—		—	—
111		4·13	ms	4·18	m	4·18	mw	4·16	4·11		ms	4·16
—		—	—	—	vvw	4·00	—	—	—		—	—
120		—	—	—	—	—	—	—	3·93		w	3·93
200		3·75	w	3·76	vw	3·78	vvw	3·78	3·71		m	3·72
210		3·47	vvw	3·49	vw	3·51	—	—	3·45		m	3·44
121		3·25	vvw	3·32	vvw	3·32 }	vvsb	3·16	{ 3·25		w	3·26
201		3·16	vvs	3·17	vvs	3·17 }			{ 3·13		vs	3·13
030		3·05	vvw	3·07	—	—	—	—	—		—	—
002		2·95	vvw	2·96	vvw	2·94	—	—	—		—	—
130	(012 ?)	2·82 (2·81)	s	2·91	s	2·91	vsb	2·87	2·92 (2·79)		vs	2·85
131		2·61 }	vsb	2·63	vsb	2·63	vsb	2·63	{ 2·62		vs	2·62
221		2·60 }							{ 2·59		ms	2·57
022		2·48	w	2·51	vw	2·52	vw	2·51	2·47		w	2·48
310	(230 ?)	2·41 (2·42)	w	2·42	vw	2·42	vvw	2·42	2·38 (2·42)		wb	2·38
202		2·32	—	—	vvw	2·32	vvw	2·33	2·30		w	2·30
212		2·25	m	2·26	mw	2·26	mw	2·25	2·23		vw	2·23
222		2·11	w	2·12 }	w	2·08	mb	2·08	{ 2·06 }		m	2·06
321		2·05	mw	2·08 }					{ 2·12 }			
132 ?		2·04	vw	2·00	—	—	—	—	—		—	—
240		1·96	vw	1·97	—	—	—	—	1·98		vw	1·97
330		1·931	vw	1·93	—	—	—	—	—		—	—
400		1·911	vw	1·91	—	—	—	—	—		—	—
312		1·867	mb	1·868	msb	1·861	msb	1·851	1·850		m	1·854
232		—	—	—	—	—	—	—	1·839		m	1·832
123		—	—	—	—	—	—	—	1·821 }		m	1·817
410		—	—	—	—	—	—	—	1·819 }			
203		1·741	m	1·750	m	1·745	ms	1·743	1·726		s	1·721
332 ?		1·616	ms	1·637	sb	1·635	s	1·630	1·608		s	1·608
402		1·582	mw	1·586	w	1·584	w	1·584	1·566		mw	1·564
			mw	1·562	w	1·559	w	1·551			mw	1·531
			w	1·483							vw	1·483
			vvw	1·464							w	1·463
			w	1·413							vw	1·441
			w	1·394							vvw	1·419
			vvw	1·359							w	1·386
			mw	1·343							vw	1·372
			mwb	1·322							vvw	1·345
											vvw	1·321
											ms	1·301

Order of decreasing intensity: vvs. vs. s. ms. m. mw. w. vw. vvw: b broad.

TABLE II. X-ray powder data in Å. for bayldonite from Cornwall.

I.	*d.*	*I.*	*d.*	*I.*	*d.*	*I.*	*d.*
m	4·92	vw	2·30	vw	1·652	vw	1·260
mb	4·54	m	2·26	mwb	1·613	vw	1·249
vw	3·36	vw	2·17	ms	1·576	vw	1·231
s	3·21	vvw	2·12	vvw	1·508	w	1·221
vvs	3·14	m	1·900	ms	1·467	vvw	1·197
ms	2·93	wb	1·872	vvw	1·449	vvw	1·178
ms	2·71	m	1·816	vvwb	1·402	vw	1·164
mw	2·65	m	1·760	vvw	1·374	wb	1·130
m	2·54	vw	1·737	wb	1·342	w	1·114
m	2·47	vw	1·716	vw	1·316	mwb	1·092
vvw	2·44	m	1·690	vw	1·272		

Order of decreasing intensities: vvs, vs, s, ms, m, mw, w, vw, vvw; b broad.
6 cm. diameter camera, Cu-$K\alpha$ radiation (λ=1·542 Å.).

X-ray investigation.

Comparative powder data for the three duftites are given in table I where they are also compared with a conichalcite from Higgins mine, Bisbee, Cochise Co., Arizona (B.M. 1924,696) (for corresponding photographs see pl. XVI, 2, 3, 4, and 6). These data are plotted on the basis of I/d in text-fig. 1. The indexing of the duftite and conichalcite patterns is based on the single crystal measurements of W. E. Richmond[1] with due regard to the obviously equivalent character of a number of the stronger lines on the two patterns. The restrictions imposed by the somewhat doubtful space-group determination for duftite have not been applied. In a few cases the assignations are uncertain. The Mapimi and Brandy Gill duftite patterns are less well resolved at higher orders than the other two.

Conichalcites from Carissa mine, Mammoth, Utah (B.M. 81763), Calavada mine, Mineral Co., Nevada (B.M. 1948,172), Tintic district, Utah (B.M. 56453 and B.M. 55627), and Congress, Yavapai Co., Arizona (B.M. 1947,267) have also been photographed and are in good agreement with the data for Higgins mine material.

In table II X-ray powder data for bayldonite (pl. XVI, fig. 1) is provided, as this does not appear to have been previously published. Bayldonites from the following localities also gave comparable patterns: St. Day United mines (B.M. 39961, 40632, 42091), Penberthy Croft mine, St. Hilary (B.M. 1905,132, and specimens belonging to Sir Arthur Russell), Wheal Carpenter (Sir Arthur Russell's specimens), and B.M. 1907,885, all from Cornwall; Tsumeb, South-West Africa (B.M. 1912,352, 1912,355,

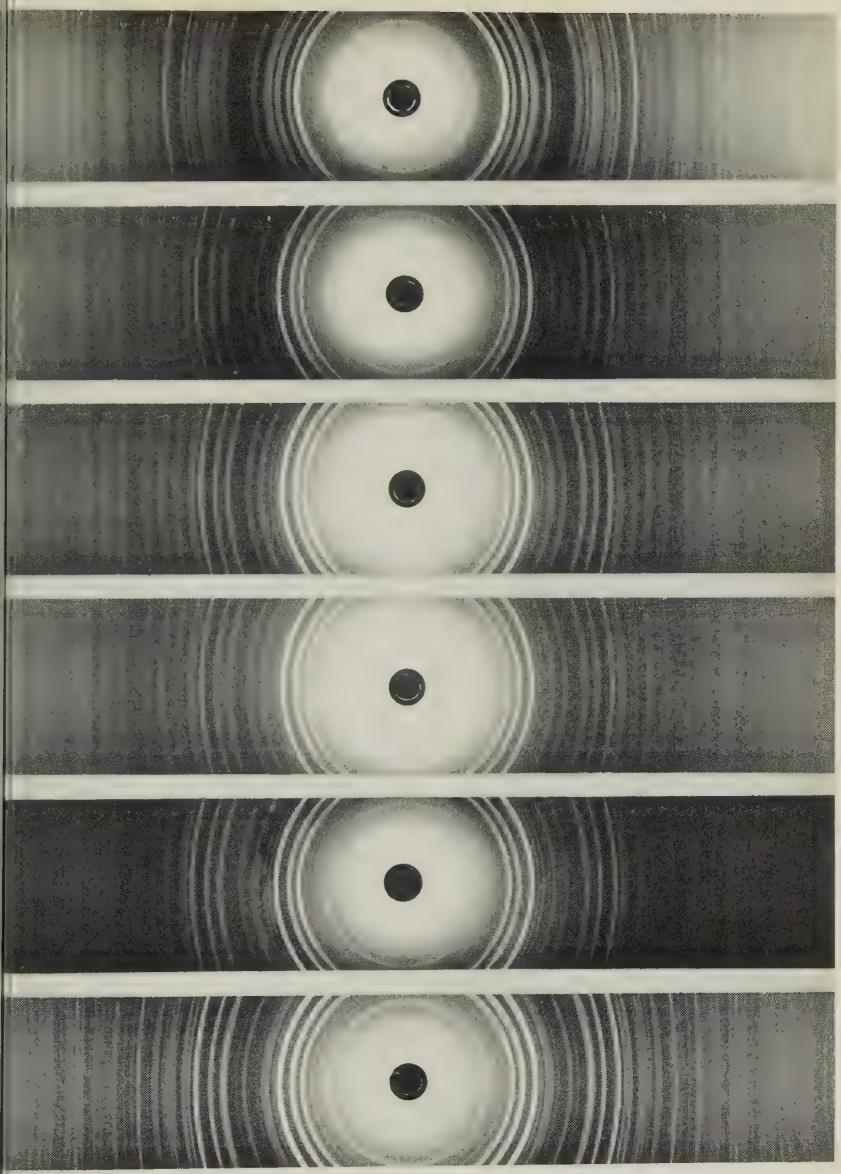
[1] W. E. Richmond, Amer. Min., 1940, vol. 25, pp. 441–479. [M.A. 8–11.]

and 1921,432); Sandbeds, Caldbeck Fells, Cumberland (B.M. 1950,445). It is hoped to publish at a later date single-crystal X-ray data for this mineral.

Explanation of Plate XVI.

X-ray powder photographs on 6-cm. diameter camera, Cu-$K\alpha$ radiation ($\lambda = 1{\cdot}542$Å.).

Fig. 1. Bayldonite, Cornwall (B.M. 1907,885).
Fig. 2. Duftite, Tsumeb, South-West Africa (B.M. 1939,225).
Fig. 3. Duftite, Ojuela mine, Mapimi, Durango, Mexico (B.M. 1948,267).
Fig. 4. Duftite, Brandy Gill, Caldbeck Fells, Cumberland (W. F. Davidson's specimen).
Fig. 5. Duftite, Brandy Gill, Caldbeck Fells, Cumberland (B.M. 1950,443). Nearer to conichalcite than fig. 4.
Fig. 6. Conichalcite, Higgins mine, Bisbee, Arizona (B.M. 1924,696).



G. F. Claringbull: X-ray photographs of duftite

On collophane in Thames gravel.

(With Plate XVII.)

By S. E. Ellis, B.Sc., F.G.S. and G. F. Claringbull, B.Sc., Ph.D., F.G.S.

Department of Mineralogy, British Museum.

[Read March 23, 1950.]

IN mid-1949 the London Natural History Society set up a committee to investigate and record temporary geological sections in the London area. Among the earliest to be dealt with was the excavation in flood-plain gravel for the foundations of the Concert Hall for the Festival of Britain (1951).[1] Samples of 100–200 grams were taken from two sand-particles for heavy mineral investigation, and material from one of these, passing 60 mesh and washed by laevigation, yielded, on separation by means of a bromoform-benzene mixture of density about 2·73, an assemblage with abundant garnet, tourmaline, zircon, and kyanite, very occasional staurolite, cassiterite, and fluorite, and moderately abundant collophane. The last-named has subsequently been found as isolated grains in the heavy or semi-heavy residues from other sand samples (including the second sample from the Concert Hall site) from the City and Westminster area. In only one other case, a sand from gravel of the same age in Bridewell Place, on the opposite bank and about half a mile down the river, has it been found in comparable abundance.

The material is extremely variable in character. It is of resinous appearance; the prevailing colour is cinnamon-brown, but it ranges to brownish-green and from deep to pale coloured. The brown colour tends to be associated with transparency and the green with opacity; some of the green grains from the Concert Hall site are translucent only at the edges. There are many inclusions, generally of deeper colour than the body of the grain and often opaque (pl. XVII, fig. 3). They may be of irregular form; some are linear, with curving branches radiating from a main axis, and seem to be due to the deposition of darker material in shrinkage cracks (fig. 2). Some semi-opaque grains show broad shrinkage

[1] B. Ainsley and S. E. Ellis, The London Naturalist, 1950, no. 29 for 1949, pp. 41, 42.

cracks filled with lighter coloured and more translucent material (fig. 3). Minute spherical or ovoidal inclusions, of darker colour and higher refractive index than the body of the grain, are common in the cinnamon-brown material. Spherulitic or pseudo-spherulitic structures (fig. 4), and a layered structure which gives rise to a tabular habit are also seen. The present boundaries of the grains cut across all such structures, so that they must have been produced by the breaking up of more massive material. Most of the grains are rounded, and such angular fragments as are found are probably (often obviously) due to the recent fracture of rounded grains. In the Bridewell Place heavy residue, colourless to very pale blue material of similar refractive index (in this case near that of crystalline apatite) is seen, which shows the relatively large Haversian canals and lacunae of mammalian bone; such material is always in unworn fragments and contrasts sharply with the rounded grains of brown or green collophane. All the forms seen (excepting the spherulitic or pseudo-spherulitic) may be either isotropic or birefringent. The latter gives vague, apparently biaxial interference figures, on one of which a negative sign was obtained. Birefringence varies from nil to about 0·005. Extinction is often irregular, but in many elongated grains it is sharp and parallel to the elongation (which is negative). Such grains are often curved and occasionally branched, the extinction direction being tangential. A submicroscopic fibrous structure is presumed from this and from the X-ray data given below.

The refractive index is extremely variable. Twenty grains were picked out of the residue from the Concert Hall site, and their range of refractive indices determined by immersion in eugenol-cinnamic aldehyde mixtures, which were measured on a Bellingham-Stanley refractometer. Nineteen grains gave values ranging 1·614–1·626 (Na-light at about 20° C.), and one (indistinguishable in general character from the others) gave a value of 1·583. Five grains from the Bridewell Place residue gave a range 1·622–1·638, while a single grain was as low as 1·585. The maximum refactive index observed is within the range of crystalline apatite and above the maximum (1·63) found by Rogers[1] for 250 determinations on fossil bone. In most cases there are perceptible variations in refractive index within the grains.

Density is also variable; of the Concert Hall material, a dozen grains (determined by suspension in methylene iodide-benzene mixtures) gave values ranging 2·78–2·90. There is no close relationship between density and refractive index; the grain of maximum refractive index (1·626)

[1] A. F. Rogers, Bull. Geol. Soc. Amer. 1924, vol. 35, pp. 535–556.

rom the Concert Hall site had a density near the minimum, and that of ·583 lay near the middle of the density range.

That the grains are minutely porous is indicated by their opacity in ir (hand-picking had to be done under xylol) and by the fact that when mounted in canada balsam they are at first opaque and only become ransparent or translucent after some hours. They dissolve with extreme lowness in acids (hydrochloric or nitric) with the evolution of gas bubbles, rom which it is presumed that carbonate is present. The quantity of aterial available did not permit of a chemical test, but its identity was roved by a composite X-ray powder photograph of six grains (X4791) hich indicated a fluor-apatite structure and was identical with photo- raphs of the collophane described by Dunham, Claringbull, and annister[1] from the Magnesian Limestone of Durham, of the apatite var. asparagus-stone) from Murcia, Spain, with which it was com- ared, and of an Iguanodon bone and shark's tooth referred to below. A single elongated grain, rotated about its long axis, gave a photograph X4787, pl. XVII, fig. 5) indicating aggregate orientation parallel to the -axis. A specimen of enamel from a mammoth tooth (referred to below) hich shows a parallel fibrous structure, gave an identical photograph X5081,) fig. 6) when rotated about the axis of elongation of the fibres.

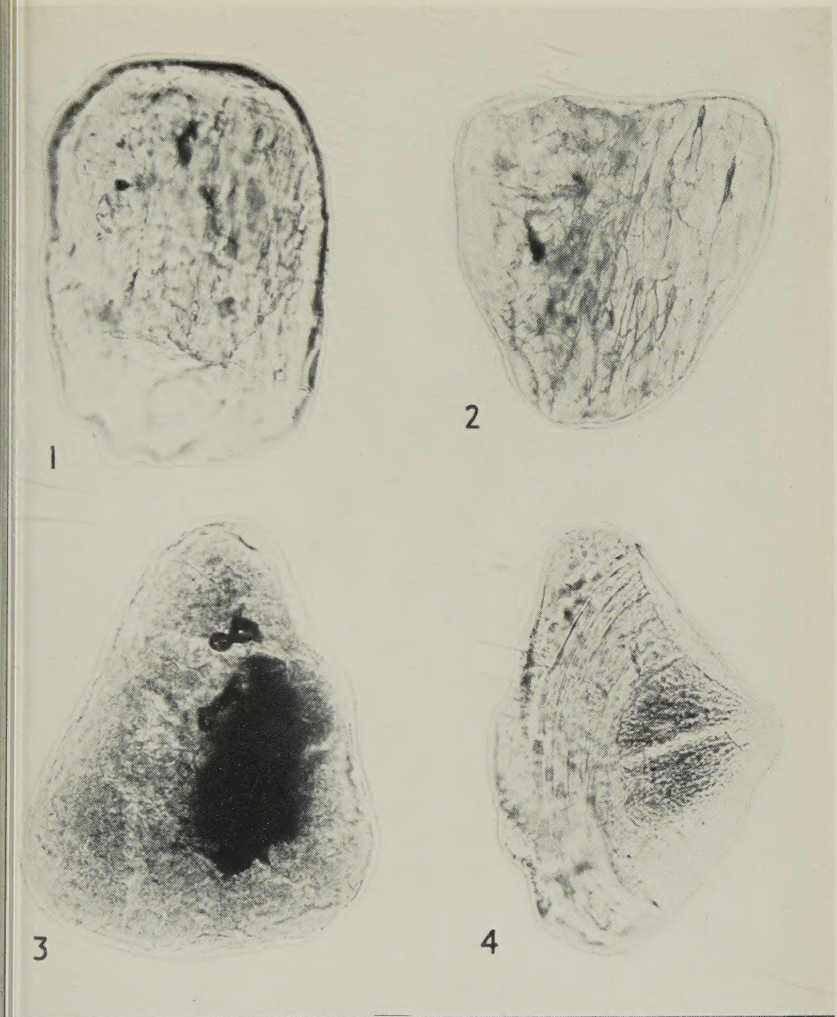
The detrital collophane was compared with a variety of forms, both of organic and inorganic origin, in the hope of throwing light on its ource. Much of the material resembles in appearance (excepting in the rounded form of the grains) that produced by powdering portions of a hosphatic nodule from the Gault clay at Sevenoaks, Kent. The latter as a similar range of densities (2·78–2·94) but a much lower refractive ndex (mean 1·6055). Reptilian bones yielded fragments similar to the rains giving extinction parallel to length. Among these, two turtle lates from the Purbeck Beds of Durlstone Bay, Dorset, have mean efractive indices (1·614 and 1·615 respectively) falling within the range f the material from the Concert Hall site, while Iguanodon bone from he Smokejacks brick pit, Ockley, Surrey, shows a lower range (1·601–1·611). These, however, are all distinctly heavier than the detrital material (density ranging up to 3·02). Some grains show a resemblance o fragments of shark's teeth, but here again there is no correspondence n refractive index and in specific gravity; dentine from the roots of two eeth of *Odontaspis macrota* (London Clay, Harefield) has a mean efractive index of 1·610 (range 1·608–1·612) and specific gravities

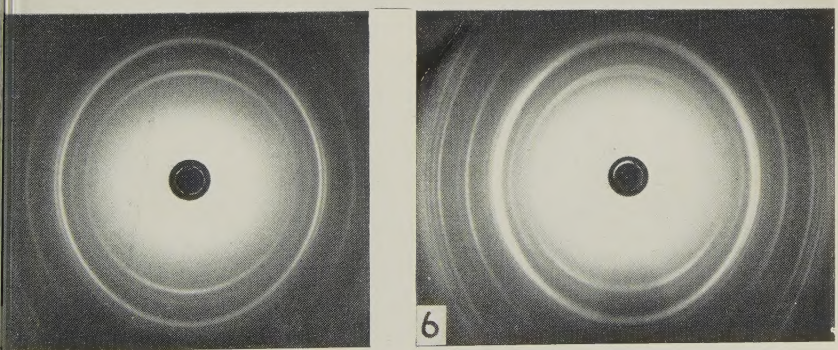
[1] K. C. Dunham, G. F. Claringbull, and F. A. Bannister, Min. Mag. 1942, vol. 28, pp. 338–343 and pl. xx, figs. 6 and 7.

ranging 2·90–3·01 and 2·96–2·99. Mammalian bones and teeth have yielded no comparable material. None of Rogers's numerous figures of thin sections of collophane shows a close likeness to the detrital material.

The failure to discover comparable material of the same refractive index does not necessarily show that the detrital collophane could not have been derived from the material it most resembles (phosphatic nodules and reptilian remains of Mesozoic age). A number of refractive index determinations on different forms of fossil bone and nodular phosphate indicate great variability, not only as between one species or occurrence and another, but within material from the same species, within a single bone or tooth and even within a single tissue of a tooth. For example, enamel from a mammoth tooth from the Doniford river gravels (late Pleistocene) of Watchet, Somerset, from which the X-ray photograph (X5081) already mentioned was taken, has a mean refractive index of 1·611 (1·606–1·616) and a specific gravity of 2·896 (solid material) at 20° C. Dentine from three different points in the same tooth has refractive index ranges of 1·583–1·586, 1·576–1·582, and 1·562–1·576 respectively, and the specific gravity does not rise above 2·60. A horn of *Bos primigenius* from the Upper Pleistocene at Gomshall, Surrey, also gave two refractive index ranges. The structure is minutely cellular and the bulk of the material is colourless with a refractive index range 1·575–1·591, but brown compact material forming cores to the cell-walls ranges 1·604–1·610. The same applies to the Gault phosphatic nodule, with a mean refractive index of 1·605, but with inclusions giving values 1·56–1·57. The existence of material of two distinct ranges has already been mentioned as characteristic of both detrital occurrences described.

Because the degree of variation is about the same, but the actual range different, in both major samples of detrital collophane, and because they are similar in other respects, the possibility has been considered that local conditions (physical and chemical) may give rise to variations in the refractive index, and in particular, that the presence of ultramicroscopic goethite in the pores may be responsible for the unusually high range of both samples, which occurred in a highly ferruginous environment. According to Rogers (loc. cit., p. 544), who admittedly bases his contention on no more than three analyses, the refractive index of fossil bones varies with the Fe_2O_3 content. It had already been observed that certain grains of collophane in the residue from the Concert Hall site, which survived digestion with hydrochloric acid (1 : 1), became very pale and suffered a reduction in the refractive index, in one case to below that of canada balsam. A few grains from the





G. F. Claringbull & S. E. Ellis: Collophane

Bridewell Place residue, with refractive indices ranging 1·622–1·634, were accordingly treated with a 10 % solution of sulphosalicylic acid, which dissolves ferric oxide readily yielding a coloured solution which can be used colorimetrically. The solution stained a filter paper faintly reddish-brown and the refractive index range of the grains was reduced to 1·605–1·615. This cannot, however, be regarded as proving that the high refractive index is due to goethite, since a specimen of mammoth dentine, which certainly contains no appreciable Fe_2O_3, had its refractive index reduced from about 1·57 to about 1·56 by the same treatment. It is, however, clear that the action of acids can lower the refractive index of collophane, though whether by the enlargement of the pores, by removal of material of high refractive index from within them, or by actual structural change is uncertain.

Since the refractive index of collophane is such a variable quantity, it can be presumed that the high values characteristic of the material described do not preclude its derivation from the phosphatic nodule beds of the Gault and from reptilian bones in the Gault and Weald Clay of the Wealden area.

In conclusion it should be mentioned that if the heavy mineral separations had been done with pure bromoform (density 2·90), instead of with a bromoform-benzene mixture of lower density, this detrital collophane would probably have passed unobserved. It is suggested, therefore, that all heavy mineral separations, at any rate of fluviatile sands, should be performed with a mixture of density of about 2·7–2·75, and that if this is done detrital collophane may prove to be much commoner than has hitherto been supposed.

Explanation of Plate XVII.

Figs. 1–4. Grains of detrital collophane from the Concert Hall site, south bank of the Thames west of Waterloo Bridge, London. Ordinary light, immersed in canada balsam. ×200.

1–3. Refractive index about 1·62; the extinction direction in fig. 1 is parallel to the longest axis of the grain.

4. Refractive index about 1·54, after reduction by digestion in HCl.

Figs. 5, 6. X-ray rotation photographs; 6 cm.-diameter camera, Cu-$K\alpha$ radiation.

5. Single grain of collophane with rotation axis parallel to extinction direction.

6. Fragment of mammoth tooth enamel with rotation axis parallel to fibrous structure.